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Chem-Eng
Soth,

FARADAY LECTURE.

(Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution, on June 12th, 1924.)

Atomism in Modern Physics.

By R. A. MILLIKAN.

IN a Faraday lecture it is fitting to attempt to analyse the present status of the struggle between continuous and discrete points of view in the interpretation of electrical and optical phenomena, for it was Faraday's experimental researches which first sharply presented the dilemma and provided both sides with their strongest arguments. In this review I shall endeavour to differentiate as carefully as may be between what may now be regarded as fact and what is still to a greater or less degree fancy.

Fifty years ago one of the most epoch-making of books produced by one of the most penetrating intellects of all time had just appeared. The author had himself contributed perhaps more than had any other single individual up to his time to the quantitative establishment of the atomic and kinetic theories of the constitution of matter. With the aid of these theories he had, among other things, predicted the scarcely credible results that the viscosities of gases should be quite the same at low pressures as at high, and that they should increase instead of decrease with temperature as do the viscosities of liquids. He had then made accurate experimental verifications of these predictions.

Yet when confronted with the problem of an atomic theory of electricity—a theory definitely suggested by Franklin more than a hundred years earlier, strikingly brought to the fore by Faraday's electrolytic discoveries of 1833, worked out in considerable detail by Wilhelm Weber in 1871, and rendered very definite in 1874 through the computation by G. Johnstone Stoney of the value of the ultimate unit of electricity, named by him seventeen years later (1891) the electron—Maxwell's amazingly keen intelligence was unconvinced.

In his text on Electricity and Magnetism published in 1873, while recognising in the chapter on Electrolysis * the significance of Faraday's laws, and even going so far as to say that "for convenience in description we may call this constant molecular charge one molecule of electricity," yet a little later on he repudiates the idea that this term can have any physical significance by saying "it is extremely improbable that when we come to understand

* I., 375—386.

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the true nature of electrolysis we shall retain in any form the theory of molecular charges, for then we shall have obtained a secure basis on which to form a true theory of electric-currents and so become independent of these provisional hypotheses."

Confronted, in other words, with the apparent irreconcilability of *dielectric* phenomena, which found their simplest interpretation in continuous quasi-elastic properties of the medium surrounding a conductor, and *electrolytic* phenomena, which suggested granules or specks of electricity sprinkled over the surface of a charged body and moving through it to produce electrical currents, Maxwell ventured the judgment that the dielectric phenomena would ultimately be found to be the more fundamental, *i.e.*, to correspond the more nearly to reality; while the electrolytic phenomena would be found to be but a seeming, and would finally be interpreted in terms of the former.

As everyone now knows, this prediction of Maxwell's has not been fulfilled. The developments of the past fifty years have been quite the opposite of what he expected. But just how far have we gone in the atomising process? How far have we overcome the difficulties seen by Maxwell? I shall begin the answer by asserting that despite an occasional doubt by a man of scientific credentials, and despite a recent statement by a prominent literary writer that "the electron is only the latest scientific hypothesis, sooner or later to be replaced by the abracadabra of to-morrow," the electron is actually no longer an hypothesis at all. It at least is a definitely and directly observable fact in terms of which dielectric phenomena must henceforth, willy-nilly, be interpreted. If anyone is disposed to question that statement let him reflect for a moment upon the following.

The definitions of positive and negative electricity are set up in terms of the familiar, classical experiments with the pith-ball, the glass rod rubbed with silk, and the ebonite rod rubbed with cat's-fur. Of the *ultimate* nature of electricity we, of course, know nothing, but we do observe directly electrical forces and by *definition* we make *quantities of electricity* on our pith balls, or other bodies, proportional to the forces exerted upon them at a particular distance from a given rubbed glass rod, *i.e.*, in a constant electrical field. To test directly the atomic theory of electricity we have then only to place, in a given electrical field, the smallest possible charge upon a very small pith ball, vary the charge by the smallest possible amounts and see whether the observed forces show any tendency to vary in a unitary way.

In the actual carrying out of this particular experiment, which was only the final step in a long chain of proof forged by many

FIG. 1.

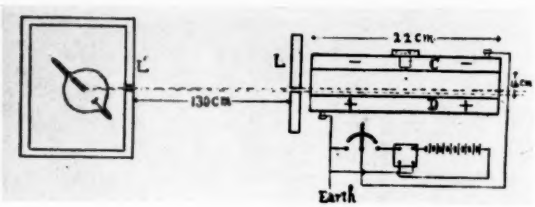

FIG. 2.

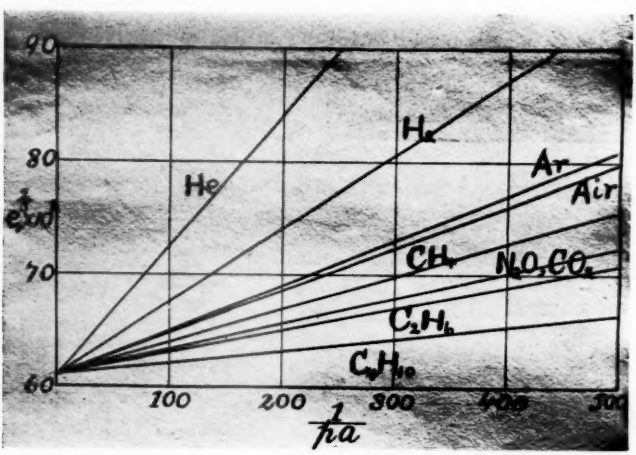

FIG. 3.

[*To face Trans., p.* 1407.]

observers, the pith ball was in fact an oil-drop about a thousandth of a millimetre in diameter but easily visible in a strong beam of light from an arc lamp, the glass rod was, of course, replaced by the constant field between the horizontal plates C and D (Fig. 1) of an air-condenser (sixteen millimetres apart) connected the one to the positive, the other to the negative, terminal of a ten-thousand volt battery, and in such a way that the field could be thrown on or off at will with a switch. The charging of the oil-drop pith-ball and the varying of its charge were accomplished in as many different ways as possible, namely, by the frictional process involved in blowing the oil-spray—this is precisely the same method as that used in charging the glass rod—, by ionising the air underneath the drop by *X*-rays, or by alpha, beta, and gamma rays from radium, and letting the field instantly throw the ions thus formed into the drop, by illuminating the surface of the droplet with both ultra-violet light and *X*-rays and letting these agencies pick off negative electricity from it as they had long been known to do, and by letting the normal kinetic energy of agitation of the ions ordinarily existing in air push these now and then against the surface of the drop, where they stick and thus change its charge.

One altogether typical result from thousands of observations made in this way is perhaps worth reviewing. When there was no field on, the oil-drop fell a given distance between the observing cross-hairs—1·303 centimetres—in an average time of 120·35 seconds. It was pulled back repeatedly to its original position by throwing on the field, the pull of the field on its charge more than equalling the downward pull of gravity.. It was then found possible to remove the charge entirely by the charge-changing agencies, and to observe that, when the ten-thousand-volt field was on, the drop now fell between the observing cross-hairs in exactly the same time, 120·3 seconds, which it took when the field was off, *thus showing that it is possible to discharge an oil-drop completely, so that it does not respond at all to electrical forces.* In other words, it is possible to make it strictly electrically neutral.

Again, it was found possible to give it a charge which caused the ten-thousand-volt field to lift it from the lower to the upper cross-hair in 67·73 seconds, and this speed could be obtained over and over again at will, by suitable manipulation of the charge-changing agency, but *no speed smaller than this could ever be found,* so long as the field-strength remained constant. The next upward speed which could be found pulled the droplet back in 26·40 seconds, and this speed too could be returned to as often as desired, but *no speed between* 67·73 *and* 26·40 could ever be obtained. The next possible upward speed was found to pull the drop back in 11·9 seconds.

In the foregoing experiment the electrical forces acting upon the droplet are strictly proportional to and hence may be taken as measured by the speeds produced. The experiment has therefore definitely proved, even if we go no farther, that electricity is not a continuum—that it is not indefinitely divisible—that it rather exists in such amounts as to permit a charge to be varied only by definite steps. But what kind of steps?

Dividing through the speeds imparted by the field in the foregoing case—this is the sum of the downward speed under gravity and the upward speed in the field—we obtain the series of numbers 0, 1, 2, 3, 4, the error being in no case more than one-third of 1 per cent.

He who has seen that experiment, and hundreds of different physicists have now seen it, has seen "*the electron.*" He has seen and measured *in terms of a speed* the smallest electrical force which is ever exerted by a constant field upon the pith-ball with the aid of the forces upon which he defines electricity itself. No object the outline of which he sees with his eyes was ever more certain or more real. Further, he has counted the precise number of electrons upon his pith-ball with quite as much certainty as he attains in counting his fingers and toes, and I have myself carried this certain counting up to about 150.

To reduce these measurements to standard electrostatic units and to learn that the value of the electron is $4{\cdot}774 \times 10^{-10}$ such units, correct to about one part in a thousand, required, it is true, thousands of such observations as the foregoing, made on many drop-substances, surrounded by many different kinds of gases, at many different pressures ranging from about $1\frac{1}{2}$ mm. to 760 mm. of mercury; it involved new and much more precise determinations of the coefficients of viscosity of gases than had previously been made, for the precision obtainable in e is limited by the precision of the measurement of this coefficient; it involved finding, through years of work only completed last year, the correct and complete law of fall which must replace Stokes' law. But the methods used in this long series of experiments are simple and altogether unquestionable. How inevitably the work on different drop-substances and in different gases converges upon the same absolute value of the electron at the intercept on the $e^{2/3}$ axis is beautifully shown in Fig. 2.*

After ten years of work in other laboratories in checking the

* This is taken from a repetition of my observations in different gases by my assistant, Dr. Yoshio Ishida. For similar observations upon different drop-substances, see "The Electron," revised ed., 1924, University of Chicago Press.

methods and the results obtained in connexion with the oil-drop investigation published from 1909 to 1923 there is practically universal concurrence upon their correctness despite the vigorous gauntlet of criticism which they have had to run.

Electrons of both the positive and negative variety are then merely observed centres of electrical force just as was the charged pith-ball from which we got our original definition of an electric charge. Up to this point we have certainly been dealing merely with observed facts and facts which the present generation of men has for the first time seen, but the consequences of which are for all time.

Again, as will presently be shown, the dimensions of both positive and negative electrons may with little uncertainty be ignored and both treated for practical purposes as point charges, though, as is well known from the investigations of Sir J. J. Thomson, Lenard, Bucherer and others, the positive certainly has a mass 1845 times that of the negative. Why this is so no one knows. It is another experimental fact.*

Not only has electricity thus been definitely atomised since Maxwell's time, but the electron has revealed itself also as the fundamental unit of atomic structure. Not all of the generally accepted elements in that structure are as definitely established as the foregoing facts, but in order to make a bridge by which to pass over now from the known to the unknown let me first summarise the points upon which practically all scientists are now agreed, and which to that extent are free from fancy.

We are all agreed that Rutherford, C. T. R. Wilson, and others have definitely shown that all the positive electricity within every atom is concentrated in the nucleus, and that the number of electrons in the outer regions of the atom is just sufficient to neutralise the free positive charge upon the nucleus.

We are all agreed that the number of free or unneutralised positive electrons in the nucleus varies from one in the case of hydrogen

* In conformity with the usage of practically all authoritative writers in all languages from 1891 up to the present I use the word electron to designate the atom of electricity or the unit electrical charge; and it seems to me highly desirable that this historically correct, etymologically most suitable, and authoritatively recognised nomenclature be retained. (See Nernst's "Theoretical Chemistry," last ed., Rutherford's 1923 B.A. address, etc.) When used without a prefix or qualifying adjective, the word electron may indeed signify if we wish, as it does in common usage, both the generic thing, the unit charge, and also the negative member of the species, precisely as the word man in English denotes both the genus homo and the male of mankind. There is no gain in convenience in replacing "positive electron" by "proton," and there is a very distinct loss, logically, etymologically, and historically.

by unit steps up to ninety-two in the case of uranium, and hence that the number of negatives held in the outer regions also varies by unit steps from one to ninety-two. This immeasurable advance was due in the first instance to the immortal Moseley.

We are all agreed that the chemical properties of all atoms, and most of the physical properties as well, mass being the chief exception, are determined by the number of these free positives contained in the nucleus.

We are all agreed that the nucleus is extraordinarily minute, so that if all dimensions were magnified ten billion times—a magnification which would make a bird-shot swell to the size of the earth, and which would also make the diameter of the atom about a meter—the nucleus on this huge scale of magnification would not be more than a tenth millimetre in diameter, that is, not larger even then than a mere pin-point.

We are all agreed, too, that in the case of uranium there are packed into that infinitesimal nucleus 238 positive and 146 negative electrons, the exact number of positives being determined by the atomic weight, while the number of negatives which bind the positives within the nucleus is the atomic weight minus the atomic number.

We are all agreed that so far as physical science has now gone there have appeared within the atom but these two fundamental entities which seem to be the building-stones of all atoms.

We are all agreed that when any of the electrons in the outer regions of the atom are stimulated to radiate they do so by virtue of falling from a level of higher potential energy to one of lower, *i.e.* from a level more remote from the nucleus to one nearer to it.

We are all agreed that the frequency of the emitted radiations is proportional, however mysterious its mechanism may still be, to the energy loss in the process of changing from the one level to the other. Indeed one of the most stimulating advances which experimental physics has made during the past six years consists in the quite complete verification of this Planck-Einstein-Bohr law of radiation. Very recent experiments of Ellis in Cambridge even go so far as to indicate that this law holds not only for the radiations emitted by the changes in energy level of the electrons outside the nucleus, but also for the radiations which originate in the nucleus itself—the so-called gamma rays—which accompany changes within the nucleus of radioactive atoms.

These results upon which we all agree are proof enough of the amazing advances which have taken place, mostly within the past fifteen years, in our ability to peer inside the atom and to see what

kind of entities exist there and what they are doing in the act of radiating.

The chief point of controversy at the moment, the point at which fact and fancy meet, has to do with how the electrons spend their leisure time, the portions of their lives within the atom when they are not radiating.

The chemist in America has in general been content with what I have called a loafer electron theory. He has imagined the electrons sitting around on dry goods boxes at every corner, ready to shake hands with, or hold on to, similar loafer electrons in other atoms.

The physicist, on the other hand, has preferred to think of them as leading more active lives, rotating with enormous speeds in orbits, and occasionally flying out of these orbits for one reason or another.

The arguments for the static electron theory are two in number. The first is that such activity as the physicist postulates would soon wear away all the energy possessed by the electrons. There is no answer to this argument. The electrons would indeed tire themselves out, provided the classical electromagnetic laws were universally applicable even in the hearts of atoms. The physicist's only answer to this argument is God did not make electrons that way. Why assume that the electromagnetic laws are universally valid when this is the first time we have had to test them out in the region of the infinitely small?

The second argument which has been advanced for the static electron theory is the existence of localised valencies in chemistry. That these localised valencies exist is admitted on all hands. But it is simply due to a misunderstanding that this argument was ever used against the orbit theory. *For no physicist—and I wish to emphasise this fact—has ever advanced the theory that the electrons all rotate in coplanar orbits.* Localised valencies are probably just as compatible with the orbit theory when the orbits are properly distributed in space, as with the conception of stationary electrons. All this I pointed out in 1916 * in an effort to clear up the misconception which existed in the minds of certain chemists as to the way in which the physicist was thinking.

Passing now to the arguments in favour of the orbit theory, it is to be observed that all of them represent definite quantitative relations which grow directly out of orbit theory and are then accurately verified experimentally.

The first was the prediction with the aid of orbit-equations of the numerical value of the Rydberg spectroscopic constant, a prediction which was found in agreement, within one part in 500,

* *Phys. Rev.*, May, 1917, read before Am. Phys. Soc., Dec. 1, 1916.

which is well within the observational error, with the directly measured value.

The second was the prediction, also from orbit theory, of a difference between the positions of two spectral lines, one due to helium, the other to hydrogen, which should theoretically coincide were it not for the fact that the helium nucleus is four times as massive as the hydrogen nucleus. It results from this that as the nucleus and its single electron rotate about their common centre of gravity both the hydrogen and the helium nucleus describe very minute circles about this centre, while the electron describes a big one, but the helium nucleus describes a smaller circle than does the hydrogen. This should theoretically cause the helium line to be slightly displaced from the hydrogen line. This displacement is actually found not only in the right direction but within a small fraction of one per cent. of the predicted amount. This experimental fact appears to be irreconcilable with any kind of a ring electron theory.

The third quantitative success of the orbit theory came when Sommerfeld showed that the Bohr theory when logically extended ought to demand two different hydrogen orbits corresponding to the second quantum state, one a circle and one an ellipse. Then by applying the relativity equation for the change in mass of the electron with its change in speed, as it moves through the portions of its orbit nearer to or remoter from the nucleus, he showed that the two orbits should have slightly different energies, and consequently that both the hydrogen and the helium lines should be doublets with the separation in the latter case sixteen times that in the former. All these results are found, when the experimental test is made, to check quantitatively with the observed facts.

A fourth quantitative argument was introduced by Epstein when he applied his amazing grasp of orbit theory to the exceedingly difficult problem of computing the perturbations in electron orbits and hence the change in energy of each due to exciting hydrogen and ionised helium atoms to radiate in an electrostatic field. He thus predicted the whole complex character of what we call " the Stark effect," showing just how many new lines were to be expected and where each one should fall, and then the spectroscope yielded in practically every detail precisely the result which the Epstein theory demanded.

A fifth quantitative success of the orbit theory is one which Mr. I. S. Bowen and the author, working at the California Institute, have just brought to light. Through creating what we call hot-sparks in extreme vacuum we have succeeded in stripping in succession one, two, three, four, five, and six of the valence or outer

electrons from the atoms studied. In going from lithium through beryllium, boron, and carbon to nitrogen we have thus been able to work with stripped atoms of all these substances. These stripped atoms constitute structures which are all exactly alike, save that the electrical fields in which the single electron which is doing the radiating is describing its orbits, increase in the ratios one, two, three, four, five as we go from stripped lithium to stripped nitrogen, for example. Now we have applied Sommerfeld's relativity-doublet formula, developed for a simple nucleus-electron system, and have found *not only that it predicts everywhere the progression of doublet separation with atomic number of the spectra produced by all these stripped atoms, but that it enables us to compute the precise effect which the two electrons close to the nucleus of all these atoms have in screening the outer rotating electron from this nucleus.*

At a sufficient distance from the nucleus these two electrons ought to neutralise exactly two of the free positive charges on the nucleus, *provided, and only provided, the forces emanating from these electrons fall off with the inverse square of the distance.* The relativity-doublet formula with this assumption and without the introduction of any arbitrary constants whatever enables us to determine what is the screening from the action of the nucleus of these two K electrons which are left in all the stripped atoms mentioned, and for sufficiently remote orbits it comes out in fact from our measured doublet-separations within one per cent. of *two. In other words, we have here another method, based definitely upon the theory of the change of the mass of the electron with speed in differently shaped orbits, which enables us to look with certainty inside the atom and to find how many electrons are in its inmost shell, and the answer is in perfect agreement with other determinations of this number.*

Again, when we examine the spectra due to the stripped atoms of the group of elements from sodium to sulphur—one electron having been knocked off from sodium, two from magnesium, three from aluminium, four from silicon, five from phosphorus, and six from sulphur—we should, of course, find that the number of screening electrons in the two inmost shells, when tested for sufficiently remote orbits, comes out two plus eight, or ten. The relativity-doublet formula when applied to our measured doublet separations of this group of stripped atoms yields indeed the value ten. *This agreement for both these cases constitutes unambiguous proof that the electrons themselves do possess at this distance coulomb fields* (i.e., *fields falling off with the inverse square of the distance*), *a result entirely incompatible with the stationary or loafer electron theory.* By this same relativity-doublet formula we have followed the increase in the screening of the two L orbits from 2 in stripped

atoms step by step up to 3·1, when the L shell has its full quota of 8 electrons as in neon and magnesium. Also Siegbahn, in work which he has just shown me, has found this stepping up from 3·1 up to its final value 3·5 for high atomic numbers, an increase occurring at just the points at which, in accordance with Bohr's conceptions, a new electron penetrates into the M shell as that shell fills out between scandium and copper to its final maximum number 18. In spite of these beautiful successes of the relativity-doublet formula, Mr. Bowen and I are forced into very serious difficulties which I will discuss elsewhere. But it hardly seems possible that these difficulties can apply to our simple limiting cases.

If, then, the test of truth in a physical theory is large success both in the prediction of new relationships and in correctly and exactly accounting for old ones, the theory of non-radiating electronic orbits is one of the established truths of modern physics. For the present at least it is truth and no other theory of atomic structure need hope to be considered until it has shown itself able to approach it in fertility. I know of no competitor which is as yet in sight. It is to be remembered, however, that all the foregoing orbital facts have been discovered when working with free atoms. Under the combined influence of two or more nuclei, as in compounds and in solids, these electronic orbits are presumably much modified, and are possibly radically altered.

The electronic and the sub-atomic worlds have thus revealed themselves with beautiful definiteness and wonderful consistency to the eye of the modern physicist. In their main outlines they are about as much hypothetical to-day as is the theory of the rotation of the earth upon its axis or of the planets around the sun. No one has ever seen either of these rotations. We have simply become possessed of a group of experimental facts which find a consistent and simple interpretation in that theory. Precisely similarly the generation of men now living has for the first time in history seen a whole new group of electronic and sub-atomic facts which fit together into a fairly simple and consistent scheme. These facts are henceforth the permanent heritage of the race. They will be added to but not subtracted from. The picture will be enlarged, its hazy outlines filled in, and some of its details modified, but it cannot be wiped out. Whatever discoveries may come, it is altogether probable that the electron will remain the unit of atomic structure just as the chemical atom, often said by the unthinking to have exploded, has actually lost, among all the changes of the past quarter century, not one whit of its reality nor of its vitality, but is rather to-day, just what it has

always been since its discovery, the ultimate unit of chemical combination.

But when we turn to the field of ether waves, to Maxwell's dielectric phenomena, all our confidence vanishes and the experimental physicist, at least, still stands puzzled and confused. Atomic conceptions have indeed invaded this field also, but at the moment in attempting to carry over the atomising process to radiation we face quite the same sort of an apparent contradiction which confronted Maxwell when he contemplated the problem of atomising electricity, save that our dilemma is even worse than his. His static dielectric phenomena would in themselves no longer bother us, but we have discovered new dielectric phenomena which do. The necessity for doing something radically new with radiation came with two discoveries made nearly twenty-five years ago. The first is that X-rays pass over all but a very small fraction, say one in a billion, of the atoms traversed by them without affecting these atoms at all, but here and there they pick out an atom from which they hurl an electron with great energy. The second is that light has the amazing property, first discovered by Lenard,* of ejecting electrons from metal surfaces with an energy which is independent of the distance of the source of the light from the metal, *i.e.*, independent of intensity.

In view of these facts, Sir J. J. Thomson in his Silliman lectures at Yale in 1903 first suggested that radiant energy is something which travels in localised bunches through space, along Faraday lines of force, which are thus conceived of as having actual physical reality.

As is well known, in 1905 Einstein combined this conception with Planck's quanta and set up the following equation to govern the transformation of radiant energy into electronic energy, $\frac{1}{2}mv^2 = h\nu - p$, where $h\nu$ is a light-quant, thought of as flying through space as a definite localised entity, doing a quantity of work p in getting the electron out of a metal and causing it to fly away with what is left of the incident light-quant as its own kinetic energy $\frac{1}{2}mv^2$. In 1914, 1915, and 1916,† after ten years of experimental work on the energies of escaping photoelectrons, I found to my own astonishment that the Einstein equation predicted all the experimental facts within the limits of experimental error, about half of one per cent., and made thus the first direct, and at that time exceptionally exact, determination of Planck's h.

That work too has had to run the gauntlet of severe criticism, but I think those who have followed the progress of physics during

* Lenard, *Ann. der Phys.*, 1902, **8**, 149.

† Millikan, *Phys. Rev.*, 1914, **4**, 73; 1915, **6**, 55; 1916, **7**, 362.

the eight years which have elapsed since its publication will agree that one of the most conspicuous achievements of this period has been the very complete verification by others of the exactness and quite general validity of that equation.

Within two years of the appearance of this first unambiguous verification of that equation Duane * and his co-workers at Harvard had not only proved its exact inverse, namely, that the highest frequency emitted by a target bombarded by electrons of kinetic energy $\frac{1}{2}mv^2$ is given by $\frac{1}{2}mv^2 = h\nu$, but had made this a very precise method of finding h.

Then D. L. Webster,† now of Stanford University, proved very precisely that characteristic X-rays begin to be stimulated when the bombarding electrons reach the energy given by $\frac{1}{2}mv^2 = h\nu$, where ν is now the frequency corresponding to an absorption edge.

Then de Broglie ‡ and Ellis § proved that the same photoelectric equation which my work had verified in the field of optics held also in the field of X-rays, the energy of the escaping electron being here measured by its deviability in a magnetic field.

Parallel with these developments has come the very full working out by Foote and Mohler, Davis and Goucher, Wood, McClennan, Horton and Davies and many others, the whole rich field of ionising and radiating potentials—work which involves in every instance the testing of the exactness of the reciprocal relation between the energy of electrons and of ether waves which is expressed by the Einstein equation or its inverse as it appears in the theory of Bohr.

But though the Einstein *equation* has been wonderfully successful, the conception of localised light-quanta out of which he got it has not yet been accepted, nor can it be until the apparent contradictions with the facts of interference have been removed.

Nevertheless a recent advance of great importance has been made. Within the year A. H. Compton ‖ of the University of Chicago has brought forward the best evidence which has yet appeared for the Thomson-Planck-Einstein conception of localised energy in light-rays. He goes a step further than Thomson, Planck, and Einstein together had gone and assumes that if these light-quanta exist, the laws of conservation of energy and of momentum will hold between the impact of a light-quant and a free electron. It results from this that monochromatic X-rays which have collided with and therefore been scattered by free

* Duane, *Phys. Rev.*, 1915, **6**, 66; *Proc. Nat. Acad.*, 1916, **2**, 90; *Phys. Rev.*, 1916, **7**, 599; **9**, 568, and 1917, **10**, 624.

† Webster, *Proc. Nat. Acad.*, 1917, **3**, 181, and **6**, 26, and 1920, **6**, 39.

‡ de Broglie, Paper before 3rd Solvay Congress, 1921.

§ Ellis, *Proc. Roy. Soc.*, 1921, **99**, 261, ebenda 1924.

‖ A. H. Compton, *Phys. Rev.*, 1923, **21**, 483; 1923, **22**, 409.

electrons will have lost in the impact some of their energy, and therefore had their energy $h\nu$ lowered by the process. He then finds that molybdenum rays scattered by carbon have their wave-length lowered approximately the predicted amount.

Ross * at Stanford checked this result by the photographic method, Compton having used the ionisation chamber method. Duane † at Harvard and his co-workers could find no trace of the Compton effect, and at the February meeting 1924 of the American Physical Society expressed the view that Compton and Ross had confused the Compton effect with a lowering in wave-length due to the energy required to take K electrons out of carbon. These two effects would, in the case of carbon, be closely overlapping and with difficulty distinguishable.

Messrs. Becker, Watson, and Smythe,‡ at the Norman Bridge Laboratory, have just repeated these scattering experiments with aluminium, which should have the Compton and Duane effects in entirely different places. In one of their photographs taken less than two months ago the alpha doublet of molybdenum was clearly shifted as a resolved pair by an amount measurable to about 1 per cent. of accuracy, and within this limit the shift was exactly predicted by Compton's equations. This seems to be unambiguous evidence for the reality of the Compton effect.

In another photograph, herewith presented (Fig. 3), though the resolution is not here sufficient to show the doublet, the plate is more reproducible, and it shows clearly both the alpha and beta lines of molybdenum shifted the correct amount. This plate also shows the Duane effect just where theoretically it should be, but in a position far removed from that of the Compton effect.

It is, then, not merely the Einstein equation which is now having extraordinary successes, but the Einstein conception as well, for it was certainly out of this conception, whether it is right or wrong, that Compton got his equation. Possibly, too, Duane, § Compton, ‖ Epstein and Ehrenfest ¶ in recent papers are making a little progress towards removing the apparent contradiction with interference, but the way is yet very dark. The times are, however, pregnant with new ideas, and atomic conceptions in the field of ether waves seem to hold at the moment the master-key to progress.

* P. A. Ross, *Proc. Nat. Acad.*, 1923, **9**, 246.
† Duane and Clark, *Proc. Nat. Acad.*, 1924.
‡ *Proc. Phys. Soc.*, April 25, 1924; see *Phys. Rev.*, June, 1924.
§ Duane, *Proc. Nat. Acad.*, 1923, **9**, 158.
‖ A. H. Compton, *Proc. Nat. Acad.*, 1923, **9**, 359.
¶ Epstein and Ehrenfest, *Proc. Nat. Acad.*, April, 1924.

CLXXVIII.—*The Isomerism of the Oximes. Part XIX. Substituted Cinnamaldoximes.*

By O. L. BRADY and H. J. GRAYSON.

PREVIOUS work on the substituted cinnamaldoximes (Brady and Thomas, J., 1922, **121**, 2098) has been extended. In view of the exceptional behaviour of *o*-methoxybenzaldoxime, the oximation of *o*-methoxycinnamaldehyde has been studied; this in alkaline solution gives with hydroxylamine the *anti*-oxime, thus resembling the nitrocinnamaldehydes rather than cinnamaldehyde. Unlike the former, however, it gives *o*-methoxycinnam*syn*aldoxime quite easily when the oximation is carried out with hydroxylamine hydrochloride in the absence of alkali. Another example of the conversion of a *syn*-aldoxime into the corresponding *anti*-isomeride through the benzoyl compound (Brady and Thomas, *loc. cit.*) has been found, since the stable *o*-methoxycinnam*syn*aldoxime on benzoylation gives benzoyl-*o*-methoxycinnam*anti*aldoxime, from which the pure *anti*-oxime can be obtained by hydrolysis.

In the earlier work, the difficulty experienced in the purification of *m*-nitrocinnam*anti*aldoxime suggested that some of the *syn*-isomeride was present, but attempts at its separation failed; it has now been found that *m*-nitrocinnam*syn*aldoxime can be prepared through the hydrochloride in the usual way. Its melting point (163°) is close to that of the *anti*-isomeride (157°), and there is little doubt that a small amount of this compound is formed in the oximation of *m*-nitrocinnamaldehyde even in the presence of alkali. *o*-Nitrocinnam*syn*aldoxime has been prepared by the usual method and evidence of the partial conversion of *p*-nitrocinnam-*anti*aldoxime into the *syn*-isomeride has been obtained.

EXPERIMENTAL.

o-*Methoxycinnam*anti*aldoxime* was prepared by adding a solution of 7 grams of hydroxylamine hydrochloride to 12 grams of the aldehyde suspended in 100 c.c. of 2*N*-sodium hydroxide, shaking until solution was complete, precipitating with carbon dioxide, and extracting with ether. After drying and removal of the solvent, the oil crystallised slowly on scratching and after pressing on a porous tile gave 10 grams of crude oxime (m. p. 60—68°). Two crystallisations from light petroleum gave the pure oxime as colourless needles, m. p. 82° (Found: N = 8·2. $C_{10}H_{11}O_2N$ requires N = 7·9 per cent.).

Acetic anhydride at 30° gave *acetyl*-o-*methoxycinnam*anti*aldoxime*, a white, crystalline powder from dilute alcohol; m. p. 82° (Found:

N = 6·5. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.). This depressed the melting point of the oxime on admixture and dissolved slowly on warming with 2*N*-sodium hydroxide, giving the sodium salt of the original oxime, thus establishing the *anti*-configuration of that compound.

o-*Methoxycinnam*syn*aldoxime*.—A solution of 20 grams of *o*-methoxycinnamaldehyde in 85 c.c. of warm alcohol was mixed with a saturated aqueous solution of hydroxylamine hydrochloride and kept over-night. On pouring into excess of 2*N*-sodium carbonate a yellow oil separated which solidified to a pasty mass. After being washed with water and dried by suction, this was stirred into an equal volume of ether, when a white, crystalline solid remained which was separated and washed with a very small amount of ether. The crude syn-*oxime* thus obtained (5 grams; m. p. 132°), on crystallisation from benzene, gave the pure compound (3 grams) in long, colourless needles, m. p. 135·5° (Found: N = 8·1. $C_{10}H_{11}O_2N$ requires N = 7·9 per cent.). It was also obtained from the *anti*-isomeride by saturating a hot chloroform solution with hydrogen chloride, when a hydrochloride was precipitated as a yellow, crystalline powder, m. p. 142° (decomp.) (Found: Cl = 16·2. $C_{10}H_{12}O_2NCl$ requires Cl = 16·6 per cent.). This on solution in 2*N*-sodium hydroxide followed by the addition of a saturated solution of ammonium chloride gave a crude *syn*-oxime (m. p. 122°) which could be purified by crystallisation from benzene.

Acetic anhydride at 30° gave *acetyl*-o-*methoxycinnam*syn*aldoxime* and not the nitrile as is usually the case (compare, however, Wentworth and Brady, J., 1920, **117**, 1045; Brady and Dunn, J., 1923, **123**, 1800). This after three crystallisations from dilute alcohol consisted of colourless, microscopic crystals, m. p. 77° (Found: N = 6·3. $C_{12}H_{13}O_3N$ requires N = 6·4 per cent.). On heating for some hours with 2*N*-sodium hydroxide, the acetyl compound dissolved, giving the salt of *o*-methoxycinnamic acid but no oxime.

Benzoyl-o-*methoxycinnam*anti*aldoxime*.—One gram of *o*-methoxycinnam*syn*aldoxime was slowly added to 5 grams of benzoyl chloride; the deep yellow solution, when stirred, deposited a quantity of crystalline material which was subsequently found to be the hydrochloride of the oxime. The whole was poured into 200 c.c. of 2*N*-sodium hydroxide, shaken, and kept over-night; the oily solid which remained was treated with a small quantity of ether, and the white, crystalline residue, which was sparingly soluble in ether, was washed with a little of this solvent, and crystallised from benzene and light petroleum. The ether solution, on

evaporating at room temperature, gave a solid and an oil; the latter was removed by suction and by draining on tile; the solid, crystallised from benzene and light petroleum, gave a product identical with the sparingly soluble compound above. Thus prepared, *benzoyl*-o-*methoxycinnam*anti*aldoxime* forms colourless, cubic crystals, m. p. 128° (Found: N = 5·5. $C_{17}H_{15}O_3N$ requires N = 5·0 per cent.). The benzoyl derivative was hydrolysed for 2 hours with hot 2*N*-sodium hydroxide; the cooled solution, saturated with carbon dioxide, deposited *o*-methoxycinnam*anti*-aldoxime as an oil which could be purified as before. The *anti*-oxime on similar treatment gave the same benzoyl derivative.

2 : 4-*Dinitrophenyl Ether of* o-*Methoxycinnam*syn*aldoxime*.—A solution of 1 gram of *o*-methoxycinnam*anti*aldoxime and 1·1 grams of 2 : 4-dinitrochlorobenzene in warm alcohol was treated with 3 c.c. of 2*N*-sodium hydroxide, a dark coloration appearing. The ether, which was precipitated after a few seconds, was washed with alcohol until free from colour and with water, and crystallised from boiling acetone or better from boiling glacial acetic acid, in both of which it was sparingly soluble. It formed pale yellow needles, m. p. 202° (decomp.) (Found: N = 12·5. $C_{16}H_{13}O_6N_3$ requires N = 12·3 per cent.). Hydrolysis with alcoholic potassium hydroxide gave 2 : 4-dinitrophenol and *o*-methoxycinnamic acid (compare Brady and Truszkowski, this vol., p. 1087).

m-*Nitrocinnam*syn*aldoxime* was prepared by two methods. A solution of the *anti*-oxime in hot benzene was saturated with hydrogen chloride, when the hydrochloride was precipitated as an amorphous, pale yellow powder, m. p. 175° (decomp.) (Found: Cl = 15·1. $C_9H_9O_3N_2Cl$ requires Cl = 15·5 per cent.). This was dissolved in 2*N*-sodium hydroxide and the oxime precipitated with ammonium chloride solution; after crystallisation from acetone and water, the *syn*-oxime was obtained as a yellow, crystalline powder, m. p. 163° (Found: N = 14·3. $C_9H_8O_3N_2$ requires N = 14·6 per cent.). When prepared by Dunstan and Thole's method (P., 1911, **27**, 233), the product after crystallisation was not quite so pure, melting at 158°. Admixture of the *syn*-oxime with the *anti*-isomeride (m. p. 157°) caused a depression of the melting point, but the entity of the new compound was established by the action of acetic anhydride. This gave a compound which on crystallisation from dilute alcohol melted at 98—100° and was apparently acetyl-*m*-nitrocinnam*syn*aldoxime, for on solution in alcohol and treatment with alcoholic potassium hydroxide it yielded *m*-nitrocinnamonitrile. Under similar conditions, the *anti*-oxime gives acetyl-*m*-nitrocinnam*anti*aldoxime (m. p. 136°), which, on hydrolysis regenerates the *anti*-oxime (Brady and Thomas, *loc. cit.*).

o-*Nitrocinnam*syn*aldoxime* was prepared by methods analogous to those employed for the *m*-nitro-compound above. The hydrochloride, precipitated from a hot benzene solution, formed a white, crystalline powder, m. p. 144° (decomp.) (Found: Cl = 15·5. $C_9H_9O_3N_2Cl$ requires Cl = 15·5 per cent.). It was decomposed by 2*N*-sodium hydroxide and the oxime precipitated with ammonium chloride solution; after crystallisation from acetone and water, the *syn*-oxime was obtained in pale yellow needles, m. p. 138°, which depressed the melting point of the *anti*-oxime (m. p. 134°) on admixture. A somewhat purer compound, obtained by Dunstan and Thole's method (*loc. cit.*), melted at 140° after crystallisation from acetone and water (Found: N = 14·8. $C_9H_8O_3N_2$ requires N = 14·6 per cent.). The configuration of the *syn*-oxime thus obtained was determined in the usual way. As in the case of the *m*-nitro-compound, the *syn*-acetyl derivative was stable to sodium carbonate solution, but on gentle hydrolysis with alcoholic sodium hydroxide it yielded *o*-nitrocinnamonitrile together with a little *o*-nitrocinnam*anti*aldoxime; the formation of the latter may indicate that the original oxime was not pure but contained some *anti*-isomeride, but it is likely that part of the acetyl compound underwent isomeric change during the manipulation.

p-*Nitrocinnam*syn*aldoxime*.—Although evidence of the formation of the *syn*-oxime has been obtained, conversion was in all cases apparently very incomplete, and the amount of material at our disposal prevented the separation of the *syn*-isomeride in the pure state. The *hydrochloride*, precipitated from hot benzene solution, consisted of a deep yellow powder, m. p. 173° (decomp.) (Found: Cl = 15·4. $C_9H_9O_3N_2Cl$ requires Cl = 15·5 per cent.). Decomposition of this hydrochloride gave an oxime melting at 140°, and after admixture with the *anti*-isomeride (m. p. 179°) at 166—168°, whilst crystallisation gave a product melting at 155°. As the *syn*-oxime almost invariably melts at a higher temperature than the *anti*-isomeride, this indicated that only partial conversion had occurred. This was confirmed by the results of the determination of the configuration of the product, since nearly as much *anti*-oxime as nitrile was obtained.

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CLXXIX.—*Some Binary Systems Composed of Acetic Acid and the Homologues of Aniline.*

By Edmund Arthur O'Connor.

An investigation (J., 1921, **119**, 401) of the binary system aniline–acetic acid established the formation of two compounds, $C_6H_5{\cdot}NH_2$, $2C_2H_4O_2$ and $2C_6H_5{\cdot}NH_2,C_2H_4O_2$, the latter of which is metastable throughout the whole range of its existence. The present communication contains for comparison the results obtained by examination of some similar systems. No compound of acetic acid with any of the homologues of aniline has been previously described.

Experimental.

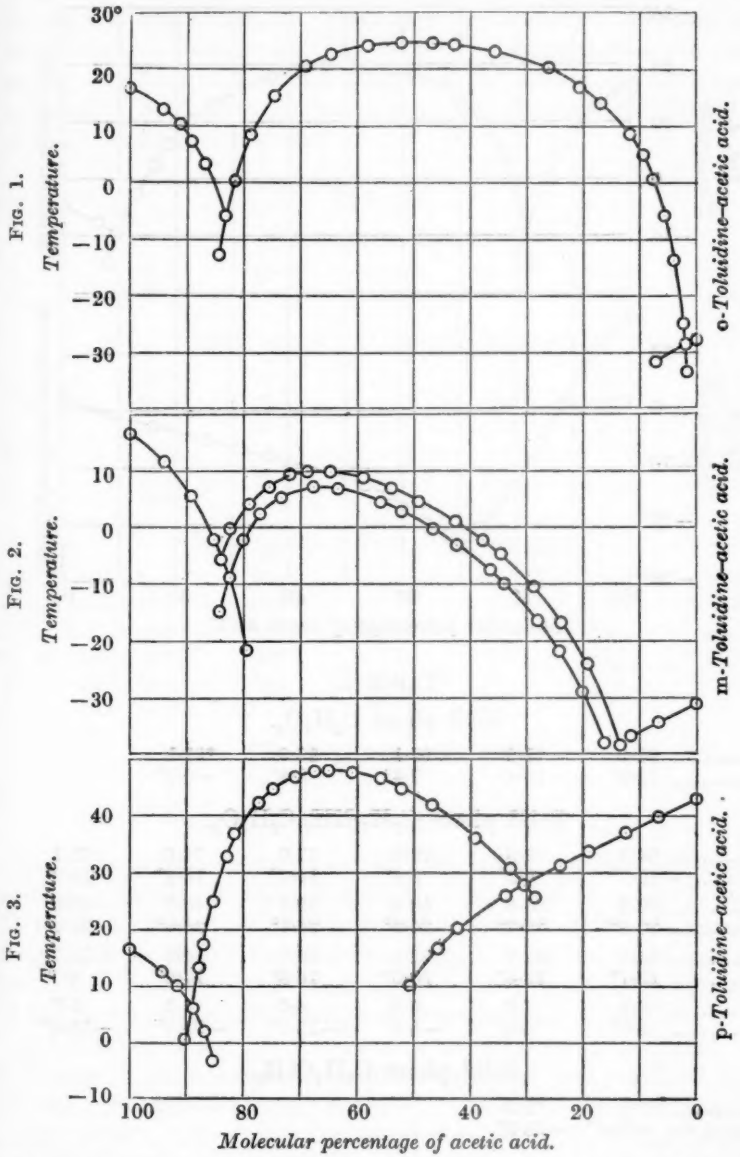
The procedure was similar to that previously adopted (*loc. cit*). In all cases a considerable amount of the solid phase or phases was allowed to separate, the composition of the liquid in equilibrium being determined by withdrawal through a filter of glass-wool and titration of the acetic acid content against standard alkali. This method is naturally more trustworthy than that usually employed in determination of freezing points, and in much of the work was essential owing to slow attainment of equilibrium between solid and liquid. Low temperatures were produced by cooling alcohol by immersing in it a bulb containing liquid ammonia, which could be boiled under reduced pressure if necessary. Reasonably constant temperatures were obtained by adjusting the rate of supply of ammonia to the bulb.

The data for the various systems are set out in the following tables, and represented graphically in Figs. 1—5. Invariant (eutectic) points are marked with an asterisk.

o-*Toluidine–Acetic Acid.*—The *o*-toluidine was purified sufficiently by crystallisation of the sulphate from hot water. The amine did not freeze until a temperature of — 55° was reached. At this point the supercooled, viscous liquid solidified on stirring. The melting point was then found to be — 27·7°, and a sample was preserved by liquid ammonia for inoculation purposes. Mixtures of a large range of composition readily deposited the compound $C_7H_7{\cdot}NH_2,C_2H_4O_2$ on strong cooling. This substance, m. p. 24·8°, was the only compound obtainable. The results are plotted in Fig. 1 and set out in the following table; *a* denotes the molecular percentage of acetic acid in the liquid phase, and *t* the temperature of equilibrium.

m-*Toluidine–Acetic Acid.*—The purification of *m*-toluidine was carried out similarly to that of the ortho-compound. It became

solid at the temperature of a mixture of solid carbon dioxide and ether, and melted at − 31·0°. The separation of the compound of



m-toluidine and acetic acid was achieved only with difficulty. It was finally obtained by continuous stirring of a mixture containing about equal parts of acid and amine in a stout glass tube kept at

— 50°. At this temperature, stirring was just possible by exercise of considerable force, the supercooled liquid being excessively

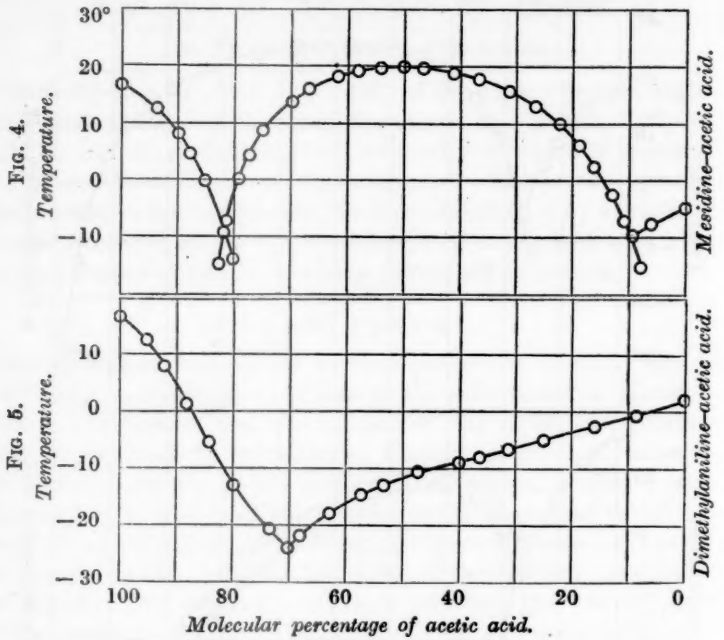


TABLE I.

Solid phase $C_2H_4O_2$.

a.....	94·4	91·2	89·1	86·6	*83·1
t.....	13·0°	10·4°	7·4°	3·4°	−5·9°

Solid phase $C_7H_7{\cdot}NH_2,C_2H_4O_2$.

a.....	84·3	81·5	78·9	77·0	74·6	72·1
t.....	−12·7°	0·3°	8·6°	11·5°	15·4°	18·2°
a.....	69·2	64·6	58·0	52·1	46·7	42·9
t.....	20·6°	22·7°	24·2°	24·7°	24·6°	24·4°
a.....	35·7	32·7	26·1	20·7	16·9	11·7
t.....	23·1°	22·4°	20·5°	16·9°	14·2°	8·7°
a.....	9·3	7·6	5·5	4·0	2·3	1·7
t.....	5·0°	0·6°	−5·8°	−13·8°	−25·0°	−33·4°

Solid phase $C_7H_7{\cdot}NH_2$.

a.....	7·1	*2·0
t.....	−31·5°	−28·5°

viscous. Once produced, a sample was preserved for seeding. The results tabulated below and plotted in Fig. 2 indicate that this compound, of composition $C_7H_7{\cdot}NH_2,2C_2H_4O_2$, exists in two

modifications, m. p.'s 10·0° and 7·3°, respectively, and that the latter is metastable with respect to the former throughout the whole range of its existence as far as investigated. The stable α-modification was first obtained. Subsequently the sample was lost, and an attempt to prepare another resulted in separation of the metastable or β-form. A second sample of the α-form was afterwards obtained. No definite conditions were discovered for the separation of either modification at will.

TABLE II.

Solid phase $C_2H_4O_2$.

a.....	93·8	89·2	85·2	*83·9	*82·4	79·3
t.....	12·0°	5·6°	−2·3°	−5·6°	−8·8°	−21·6°

Solid phase α-$C_7H_7{\cdot}NH_2,2C_2H_4O_2$.

a.....	82·3	79·0	75·4	71·9	68·7	64·8
t.....	−0·2°	4·0°	7·2°	9·4°	9·9°	9·9°
a.....	58·9	54·0	49·1	42·5	37·7	34·5
t.....	8·9°	7·0°	4·5°	1·0°	−2·3°	−4·8°
a.....	28·6	23·8	19·1	13·5		
t.....	−10·5°	−16·8°	−24·0°	−38·5°		

Solid phase β-$C_7H_7{\cdot}NH_2,2C_2H_4O_2$.

a.....	84·2	80·0	77·0	73·3	67·6	63·3
t.....	−14·8°	−2·2°	2·3°	5·3°	7·2°	6·9°
a.....	55·8	52·1	46·6	42·3	36·4	34·0
t.....	4·5°	2·8°	−0·3°	−3·1°	−7·5°	−10·0°
a.....	28·0	24·1	20·0	16·1		
t.....	−16·3°	−21·9°	−29·0°	−38·0°		

Solid phase $C_7H_7{\cdot}NH_2$.

a.....	11·5	6·6
t.....	−36·8°	−34·3°

The invariant points α-$C_7H_7{\cdot}NH_2,2C_2H_4O_2$–$C_7H_7{\cdot}NH_2$–liquid and β-$C_7H_7{\cdot}NH_2,2C_2H_4O_2$–$C_7H_7{\cdot}NH_2$–liquid lie at − 37·7° and 13 per cent. and at − 39·0° and 16·0 per cent. acetic acid, respectively. These values were inferred from the curves, as it was extremely difficult to obtain them directly owing to the high viscosity of the liquid phase, and consequent trouble in its separation.

p-*Toluidine–Acetic Acid.*—Pure *p*-toluidine was prepared by reduction of the corresponding nitro-compound, recrystallised from alcohol. It melted sharply at 43·0°. Owing to the high melting point (48·0°), the only compound formed ($C_7H_7{\cdot}NH_2,2C_2H_4O_2$) separated easily, but lengthy metastable prolongations of the curves for acetic acid and *p*-toluidine as solid phases were obtained. The results are given in Table III and Fig. 3.

TABLE III.

Solid phase $C_2H_4O_2$.

a.....	94·3	91·5	*88·9	86·8	85·4	
t.....	12·6°	10·1°	6·1°	2·0°	−3·1°	

Solid phase $C_7H_7{\cdot}NH_2,2C_2H_4O_2$.

a.....	90·3	87·7	87·0	85·2	82·8	81·5
t.....	0·6°	13·3°	17·5°	25·0°	32·8°	36·8°
a.....	77·2	74·9	70·7	67·4	65·1	60·9
t.....	42·2°	44·6°	46·8°	47·8°	48·0°	47·6°
a.....	55·9	52·1	46·8	39·1	32·8	28·5
t.....	46·6°	44·8°	41·8°	36·0°	30·7°	25·7°

Solid phase $C_7H_7{\cdot}NH_2$.

a.....	50·7	45·7	42·3	33·8	*30·4	24·0
t.....	10·2°	16·7°	20·2°	26·0°	27·9°	31·3°
a.....	19·0	12·5	6·7			
t.....	33·7°	37·0°	39·8°			

Mesidine–Acetic Acid.—Pure mesidine was prepared from a recrystallised sample of nitromesitylene by reduction with boiling stannous chloride solution. It exhibited a far greater degree of supercooling than aniline, but froze readily at the temperature of liquid ammonia. It melted constantly at −4·9°. The compound with acetic acid, $C_9H_{11}{\cdot}NH_2,C_2H_4O_2$, m. p. 18·9°, separated quite easily—readily enough to prevent any metastable prolongation of the curve for mesidine as solid phase being obtained. The numerical results are contained in Table IV, and are represented graphically in Fig. 4.

TABLE IV.

Solid phase $C_2H_4O_2$.

a.....	93·6	89·8	87·9	85·1	*81·7	80·0
t.....	12·3°	8·1°	4·6°	0·1°	−9·3°	−13·9°

Solid phase $C_9H_{11}{\cdot}NH_2,C_2H_4O_2$.

a.....	82·5	81·3	79·2	77·4	74·9	69·8
t.....	−14·7°	−7·2°	0·1°	4·3°	8·7°	13·8°
a.....	66·8	61·7	58·1	54·1	50·1	46·2
t.....	16·0°	18·2°	19·1°	19·7°	19·9°	19·7°
a.....	41·1	36·7	31·3	26·6	22·4	18·8
t.....	18·9°	17·8°	15·7°	13·1°	10·0°	6·1°
a.....	16·2	13·0	10·9	7·9		
t.....	2·4°	−2·5°	−7·1°	−15·9°		

Solid phase $C_9H_{11}{\cdot}NH_2$.

a.....	*9·4	6·0	
t.....	−9·6	−7·7°	

Dimethylaniline–Acetic Acid.—The dimethylaniline, after drying and distillation, was found to freeze constantly at 2·2°, and was taken to be sufficiently pure. No compound with acetic acid

separated as a solid phase, the equilibrium diagram (Fig. 5) being of the simplest form. The data are set out in Table V.

TABLE V.

Solid phase $C_2H_4O_2$.

a.....	95·7	92·2	88·2	84·3	79·8	73·4
t.....	12·6°	7·9°	1·3°	−5·5°	−13·0°	−20·7°
a.....	70·1					
t.....	−24·0°					

Solid phase $C_6H_5{\cdot}NMe_2$.

a.....	68·0	62·8	57·4	53·3	47·3	40·0
t.....	−21·8°	−18·0°	−14·7°	−13·0°	−10·6°	−9·0°
a.....	36·2	31·4	24·9	15·9	8·5	
t.....	−8·1°	−6·7°	−5·0°	−2·7°	−0·7°	

Conclusions.

The foregoing data indicate that primary aromatic amines containing no methyl group in the ortho-position to the amino-group combine, like aniline, with acetic acid in the molecular ratio 1 amine : 2 acid. Those containing a methyl group in the ortho-position combine in the ratio 1 amine : 1 acid. This result was observed first with *o*-toluidine, and the work was then repeated with mesidine in order to confirm it. The difference in behaviour may probably be ascribed to steric hindrance. The compound $2C_6H_5{\cdot}NH_2,C_2H_4O_2$ seems to be of a type peculiar to aniline. The results with dimethylaniline were somewhat unexpected. Not only did no solid compound separate, but the complexes of the tertiary amine and acid lacked the viscosity at low temperatures characteristic of those containing primary amines, and the solid phase invariably separated with great ease. Moreover, when the two liquids were mixed, the heat evolution was extremely small, in contrast to the very evident rise in temperature observed in all the other cases. Apparently the two substances are only slightly combined even in the liquid phase.

An attempt was made to investigate the system methylaniline–acetic acid, but although combination obviously took place, as indicated by the rise of temperature on mixing the liquids, it was found quite impossible to induce any solid phase other than acetic acid to separate out. The separation of acetic acid was possible only with complexes rich in that component, and all others, as well as pure methylaniline, became more and more viscous with falling temperature, forming a hard, brittle, amorphous substance when cooled by liquid air.

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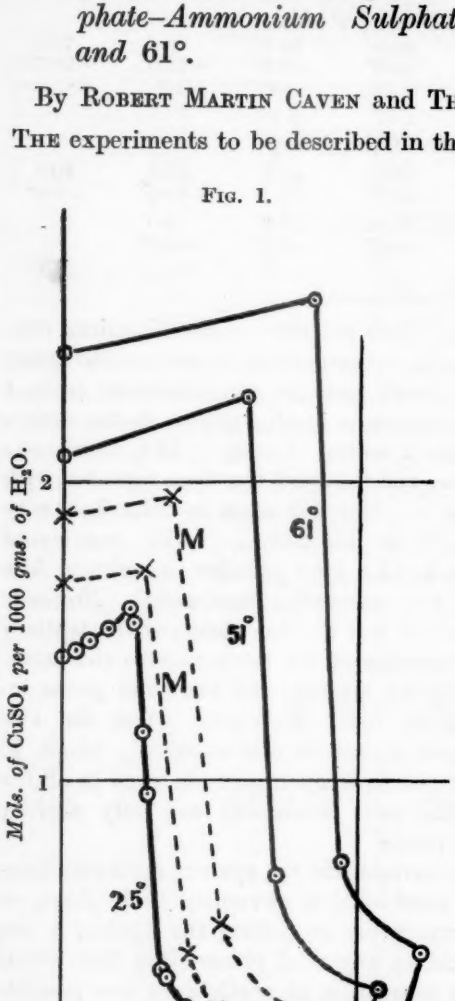
CLXXX.—*Equilibrium in the Systems Cupric Sulphate–Potassium Sulphate–Water and Cupric Sulphate–Ammonium Sulphate–Water at 25°, 51°, and 61°.*

By Robert Martin Caven and Thomas Corlett Mitchell.

The experiments to be described in the present paper were undertaken to determine the limits of existence of the double salts cupric potassium sulphate and cupric ammonium sulphate in equilibrium with their component salts and water, and also to discover evidence of the existence of these double salts in solution.

Fig. 1.



As to the first system, Rüdorff (*Pogg. Ann.*, 1873, **148**, 455) stated that each component diminished the solubility of the other. This was denied by Trevor (*Z. physikal. Chem.*, 1891, **7**, 468), who, however, concluded that no double salt existed in solution. The system was examined at 30° and 40° by Meerburg (Gedenkboek aangeboden aan J. M. van Bemmelen, 1910, p. 356); and Locke (*Amer. Chem. J.*, 1901, **27**, 459) determined the solubility of the double salt at 25°. The second system was examined at 0° by Engel (*Compt. rend.*, 1886, **102**, 113), and at 30° by Schreinemakers and de Baat (*Z. physikal. Chem.*, 1909, **66**, 693), whilst Locke

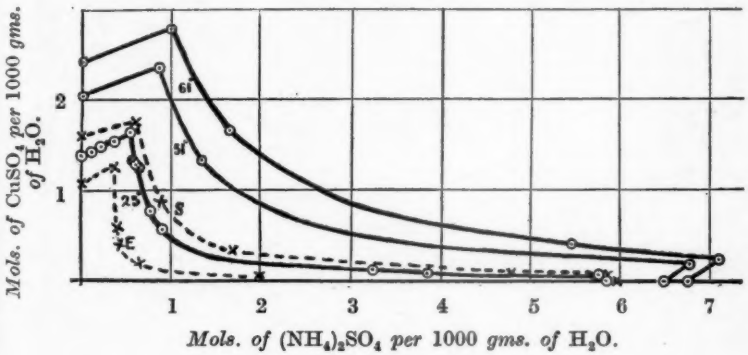
(*loc. cit.*) stated that the double salt did not exist in solution at 25°.

Experimental.

Preliminary experiments showed that the double salt $CuSO_4,M_2SO_4,6H_2O$ separates at 25° from solutions in which the ratio Cu : 2K is between 6 : 1 and 1 : 6, or the ratio Cu : $2NH_4$ between 2·5 : 1 and 1 : 60.

The solubility measurements were made at 25°, 51°, and 61°. The complexes were made up in stoppered bottles, of which three series were taken, containing, respectively, one or other component, or the double salt, as the solid phase. These were heated

Fig. 2.



in a thermostat for several weeks, being frequently shaken, and samples of the solution were withdrawn at intervals through a filter for analysis. The total sulphate was determined, and the copper estimated with iodine and thiosulphate. When two consecutive analyses agreed, equilibrium was regarded as established. With the cupric potassium salt at 61°, slight hydrolysis occurred on long standing, and an insoluble basic salt was deposited.

The results are tabulated below, and are plotted on Figs. 1 and 2, those of Meerburg for the potassium salt at 30° and 40°, and those, for the ammonium salt, of Schreinemakers and de Baat at 30°, and of Engel at 0°, being indicated by dotted lines.

Results.

C = Cupric sulphate. K = Potassium sulphate. A = Ammonium sulphate. D = Double salt.

Temperature 25°.

Mols. of $CuSO_4$ per 1000 gms. of H_2O.	Mols. of K_2SO_4 per 1000 gms. of H_2O.	Solid phase.	Mols. of $CuSO_4$ per 1000 gms. of H_2O.	Mols. of $(NH_4)_2SO_4$ per 1000 gms. of H_2O.	Solid phase.
1·410	nil.	C	1·410	nil.	C
1·415	0·014	C	1·470	0·096	C
1·430	0·037	C	1·486	0·121	C
1·457	0·086	C	1·494	0·158	C
1·477	0·110	C	1·513	0·183	C
1·504	0·150	C	1·558	0·293	C
1·570	0·225	C & D	1·646	0·534	C & D
1·525	0·228	D	1·413	0·572	D
1·149	0·261	D	1·368	0·575	D
0·955	0·270	D	1·259	0·601	D
0·365	0·331	D	0·779	0·779	D
0·350	0·350	D	0·565	0·897	D
0·237	0·412	D	0·507	0·989	D
0·120	0·598	D	0·112	3·233	D
0·092	0·737	D & K	0·070	3·826	D
0·060	0·708	K	0·051	5·715	D
nil.	0·661	K	0·042	5·762	D & A
			nil.	5·801	A

Temperature 51°.

2·073	nil.	C	2·073	nil.	C
2·266	0·618	C & D	2·365	0·861	C & D
0·677	0·706	D	1·302	1·351	D
0·312	1·036	D & K	0·180	6·733	D & A
nil.	0·923	K	nil.	6·462	A

Temperature 61°.

2·419	nil.	C	2·419	nil.	C
2·586	0·838	C & D	2·753	0·998	C & D
0·728	0·932	D	1·631	1·695	D
0·422	1·187	D & K	0·396	5·387	D
nil.	1·064	K	0·249	7·079	D & A
			nil.	6·714	A

Summary and Discussion.

The double salts $CuSO_4,M_2SO_4,6H_2O$ (M = K or NH_4) are stable at all temperatures over a wide range of relative concentrations of the components; at 25° the potassium salt is stable for ratios Cu : 2K between 7 : 1 and 1 : 8, and the ammonium salt for ratios Cu : $2NH_4$ between 3 : 1 and 1 : 137. The solubility of each of the three simple salts is continuously increased by the addition of the second component up to the triple point, at which point the double salt separates. The increase is an indication of the presence of a considerable amount of the double salt (or its ions) in solution, as was pointed out by Koppel (*Z. physikal. Chem.*, 1905, **52**, 385).

It has been observed in many cases (*e.g.*, addition of ammonium chloride to ferrous chloride, Roozeboom, *ibid.*, 1892, **10**, 145; and of potassium iodide to lead iodide, Schreinemakers, *ibid.*, 1893, **11**, 75).

Koppel himself examined the double sulphates of this type formed by sodium sulphate with a series of bivalent metals, and observed this increase with the sodium sulphate in every instance, but with the sulphate of bivalent metal only in the case of iron.

This increase of the solubility of the components is obviously connected with the unusual range of stability of the double salt, both indicating the presence of sensible amounts of the salt in solution, a fact of which one of us hopes soon to produce independent evidence.

We desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us (T. C. M.) to participate in the work.

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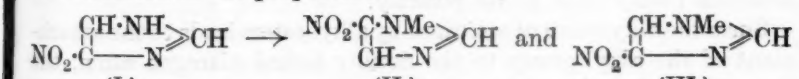
[*Received, May 2nd*, 1924.]

CLXXXI.—*The Tautomerism of Amidines. Part IV. The Methylation of 4(or 5)-Nitroglyoxaline and 4(or 5)-Phenylglyoxaline.*

By CHARLES EDGAR HAZELDINE, FRANK LEE PYMAN, and (the late) JOHN WINCHESTER.

IN connexion with the inquiry (J., 1923, **123**, 3359 and earlier) into the influence of various substituents on the relative proportions of the two isomeric alkyl derivatives produced by the action of alkyl esters upon amidines, the action of methyl sulphate upon a number of derivatives of glyoxaline with nitro-, bromo-, and phenyl-substituents has been studied. It has been found that substances containing the nitro-group in the 4(or 5)-position invariably yield as the main product the 5-nitro-1-methyl derivative.

Thus, methylation of 4(or 5)-nitroglyoxaline (I) leads to *5-nitro-1-methylglyoxaline* (II) and *4-nitro-1-methylglyoxaline* (III), which were isolated in the proportions of 350 : 1,



(I.) (II.) (III.)

and 5(or 4)-nitro-4(or 5)-methylglyoxaline gave 5-nitro-1 : 4-dimethylglyoxaline and 4-nitro-1 : 5-dimethylglyoxaline in the

proportions of 233 : 1 (J., 1922, **121**, 2616), whilst the methylation of 2-bromo-5(or 4)-nitro-4(or 5)-methylglyoxaline (J., 1923, **123**, 494), 5(or 4)-bromo-4(or 5)-nitroglyoxaline,* and 4(or 5)-nitro-5(or 4)-*p*-nitrophenylglyoxaline gave the methyl derivatives with NO_2 : Me as 5 : 1 as the sole isolable products.

The influence of the bromine atom is similar to, but not so powerful as, that of the nitro-group, for 4(or 5)-bromoglyoxaline yields 5-bromo-1-methylglyoxaline and 4-bromo-1-methylglyoxaline in the proportions of about 34 : 1, whilst the influence of the bromine atom is completely overshadowed by that of the nitro-group in the methylation of 5(or 4)-bromo-4(or 5)-nitroglyoxaline.* That the carbonyl group has an influence similar to those of nitro- and bromo-substituents appears very probable from the results of alkylating xanthines (J., 1923, **123**, 367), but this matter will be investigated later.

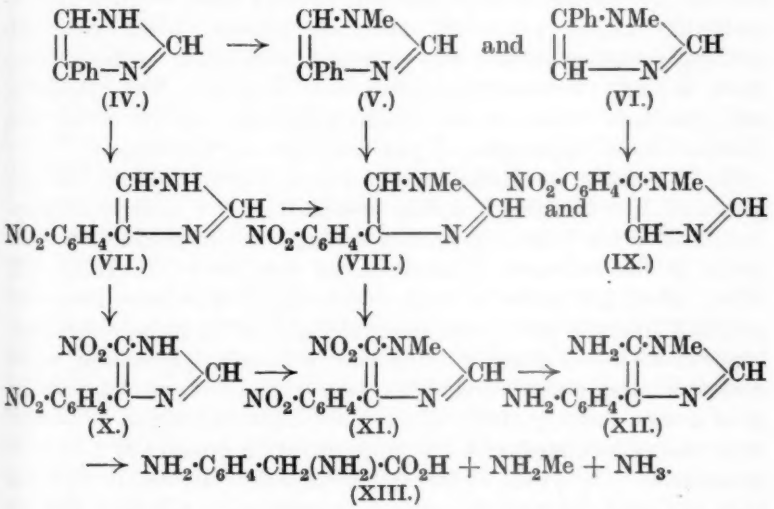
Substituents of positive polarity thus favour the formation of the 5 : 1- rather than 4 : 1-methyl derivatives, whereas those of negative polarity, such as methyl and cyanomethyl, act in the opposite way (J., 1922, **121**, 2616). The influence of a phenyl substituent, however, is exceptional, for it has been found that 4(or 5)-phenylglyoxaline (IV) yields on treatment with methyl sulphate 4-*phenyl*-1-*methylglyoxaline* (V) and 5-*phenyl*-1-*methylglyoxaline* (VI) in the proportions of 4·8 : 1. On the other hand, the influence of the phenyl group is found to be similar to that of the nitro- and bromo-groups in affecting the results of the distillation of the common methiodides of 4- and 5-substituted-1-methylglyoxalines. Thus, distillation of 4(or 5)-nitro-1 : 3-dimethylglyoxalinium iodide (obtained by the action of methyl iodide on either 4- or 5-nitro-1-methylglyoxaline) yields 4-nitro-1-methylglyoxaline almost homogeneously, 4(or 5)-bromo-1 : 3-dimethylglyoxalinium iodide yields 4-bromo-1-methylglyoxaline with a little 5-bromo-1-methylglyoxaline, whilst 4(or 5)-phenyl-1 : 3-dimethylglyoxalinium iodide yields 4-phenyl-1-methylglyoxaline with a small quantity of 5-phenyl-1-methylglyoxaline. The influence of the phenyl group on the glyoxalinium-ion is thus similar to that of the other groups of positive polarity, nitro and bromo. Its abnormal influence on the non-ionised glyoxaline molecule may be ascribed to its effect on the structure of the molecule rather than to its polarity.

Since the alkylation of amidines by alkyl esters leads to the attachment of the alkyl group to the doubly linked nitrogen atom, the formation of 4-phenyl-1-methylglyoxaline as the main product of methylation indicates that the parent substance has reacted

* Balaban and Pyman, future communication.

mainly as 5-phenylglyoxaline, $\begin{matrix}\mathrm{CPh{\cdot}NH}\\ \|\\ \mathrm{CH{-\!\!-}N}\end{matrix}\!\!>\!\mathrm{CH}$, and it is possibly significant that in this form the phenyl group is attached to the terminal member of a conjugated system.

The orientation of the 4- and 5-nitro-1-methylglyoxalines was determined by the method described previously for the nitro-1 : 4- and -1 : 5-dimethylglyoxalines (J., 1922, **121**, 2616). The methyl derivative which gave glycine, ammonia, and methylamine on reduction and hydrolysis was clearly 5-nitro-1-methylglyoxaline, and there remained for the isomeric base only the constitution of 4-nitro-1-methylglyoxaline. These two nitro-compounds were also prepared simultaneously by the nitration of 1-methylglyoxaline, when more than twice as much of the 4-nitro- as of the 5-nitro-compound was obtained. The differences in physical properties between 5-nitro- and 4-nitro-1-methylglyoxaline are paralleled by the differences between 5-nitro-1 : 4-dimethylglyoxaline and 4-nitro-1 : 5-dimethylglyoxaline (J., 1922, **121**, 2616), and their 2-bromo-derivatives (J., 1923, **123**, 493).



The orientation of the 4- and 5-phenylglyoxalines was determined by the following operations. The two bases were nitrated, when the main products were 4-p-*nitrophenyl*-1-*methylglyoxaline* (VIII) and 5-p-*nitrophenyl*-1-*methylglyoxaline* (IX) respectively, the positions of the nitro-groups being proved by the formation of a mixture of the two bases by methylation of 4(or 5)-*p*-nitrophenylglyoxaline (VII) (Grant and Pyman, J., 1921, **119**, 1893). Further nitration of 4-*p*-nitrophenyl-1-methylglyoxaline gave

5-nitro-4-p-*nitrophenyl*-1-*methylglyoxaline* (XI), the position of the second nitro-group being shown by the formation of this base by methylation of 4(or 5)-nitro-5(or 4)-*p*-nitrophenylglyoxaline (X). The dinitro-base gave on reduction *5-amino*-4-p-*aminophenyl*-1-*methylglyoxaline* (XII), which produced on hydrolysis *p*-aminophenylaminoacetic acid (XIII), methylamine, and ammonia, whence the relative positions of the methyl and phenyl (or substituted phenyl) groups in the above compounds follow.

EXPERIMENTAL.

The 4- and 5-Nitro-1-methylglyoxalines.

A. *Preparation by Nitration of 1-Methylglyoxaline.*—To a solution of 4·0 grams of 1-methylglyoxaline in 8 c.c. of concentrated nitric acid, cooled below 0°, 8 c.c. of concentrated sulphuric acid were added, when a vigorous reaction took place. After boiling gently for 2 hours, when nitrous fumes were evolved, the mixture was poured into water, basified, and extracted with chloroform. The extract (3·2 grams) was crystallised first as base, when 4-nitro-1-methylglyoxaline separated, then as picrate, when 5-nitro-1-methylglyoxaline picrate was obtained, and again as base, when more 4-phenyl-1-methylglyoxaline was isolated. The yields of pure products were 4-nitro-1-methylglyoxaline, 21 per cent., and 5-nitro-1-methylglyoxaline 8 per cent. of the theoretical.

B. *Preparation by Methylation of 4(or 5)-Nitroglyoxaline.*—Thirty grams of 4(or 5)-nitroglyoxaline and 25·3 c.c. of methyl sulphate were heated for ½ hour in boiling water, and the products worked up as in the analogous case described previously (J., 1922, **121**, 2616), when 3·8 grams of 4(or 5)-nitroglyoxaline were recovered and 52·3 grams of pure 5-nitro-1-methylglyoxaline picrate obtained, together with 0·07 gram of crude 4-nitro-1-methylglyoxaline, which melted at about 110°, and, after two crystallisations from water, gave a very small quantity of the pure base, melting at 133—134° (corr.) alone or mixed with the main nitration product of 1-methylglyoxaline. The yields of the two methyl derivatives are 63·4 and 0·24 per cent. of the theoretical, respectively, allowing for the unchanged material, but the latter figure refers to the crude product. In another experiment, when larger quantities were employed and a different method of separation was used, the yields of the two pure products were 62·3 and 0·18 per cent., respectively, the ratio between the two being about 350 : 1.

4-Nitro-1-methylglyoxaline crystallises from water in colourless, irregular spikes, m. p. 133—134° (corr.). It is sparingly soluble in cold water, and very sparingly soluble in ether, but readily

soluble in alcohol, acetone, or chloroform. Its aqueous solution is neutral to litmus (Found: C = 38·2; H = 4·1; N = 32·7. $C_4H_5O_2N_3$ requires C = 37·8; H = 3·9; N = 33·1 per cent.).

The *hydrochloride* crystallises from concentrated hydrochloric acid in large, colourless prisms, which lose hydrogen chloride and yield the base on heating at 100°. The base does not yield a picrate in aqueous solution.

5-*Nitro*-1-*methylglyoxaline* crystallises from ether in large, colourless prisms, m. p. 55° (corr.). It is readily soluble in water or ether, and very readily soluble in alcohol, acetone, or chloroform. Its aqueous solution is neutral to litmus (Found: C = 38·0; H = 4·0; N = 33·4. $C_4H_5O_2N_3$ requires C = 37·8; H = 3·9; N = 33·1 per cent.).

The *hydrochloride* crystallises from aqueous alcohol in small, glistening, colourless prisms, which contain rather more than $2H_2O$, and melt and effervesce at 195° (corr.) after drying at 100°. It is easily soluble in water, giving a strongly acid solution (Found: in air-dried salt, H_2O = 20·3; in salt dried at 100°, Cl = 21·8. $C_4H_5O_2N_3,HCl,2H_2O$ requires H_2O = 18·0 per cent. $C_4H_5O_2N_3,HCl$ requires Cl = 21·7 per cent.).

The *picrate* crystallises from water in yellow needles which are anhydrous and melt at 153·5° (corr.). It is soluble in about 25 parts of boiling water, but almost insoluble in cold water (Found: C = 34·0; H = 2·3. $C_4H_5O_2N_3,C_6H_3O_7N_3$ requires C = 33·7; H = 2·2 per cent.).

Reduction of 5-*Nitro*-1-*methylglyoxaline*.—Six grams of this base were reduced with 29 grams of hydrated stannous chloride in concentrated hydrochloric acid below 30°, and the solution was boiled gently under reflux for ½ hour.* After removing tin by means of hydrogen sulphide, the remaining hydrochlorides were mixed with sodium hydroxide, and distilled into dilute hydrochloric acid; the hydrochlorides of the volatile amines were separated by absolute alcohol into 2·6 grams of ammonium chloride (Found: Cl = 66·0. Calc., Cl = 66·3) and 2·6 grams of a soluble material, which melted at about 190° and consisted mainly of methylamine hydrochloride (Found: Cl = 53·2. Calc., Cl = 52·5 per cent.). The non-volatile residue from the distillation was acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. The extract was boiled in presence of hydrogen chloride and

* The object of boiling the solution was to complete the hydrolysis of the presumed intermediate products 5-amino-1-methylglyoxaline and glycine-*N*-methylamidine. Preliminary attempts to isolate these substances by applying the methods which were successful in the case of the reduction of 5-nitro-1 : 4-dimethylglyoxaline gave only traces of crystalline products.

concentrated, when 0·5 gram of the hydrochloride of glycine ethyl ester separated. After crystallisation from absolute alcohol, this salt melted at 144° (corr.) alone or mixed with a synthetic specimen, and its identity was further confirmed by analysis (Found : C = 34·1 ; H = 7·1 ; Cl = 25·2. Calc., C = 34·4 ; H = 7·2 ; Cl = 25·3 per cent.).

4(*or* 5)-*Nitro*-1 : 3-*dimethylglyoxalinium iodide* was obtained by heating methyl iodide with 5-nitro-1-methylglyoxaline under reflux, or with 4-nitro-1-methylglyoxaline at 100°. It forms bright yellow, serrated spikes (from alcohol), which melt and effervesce at 181° (corr.) after sintering earlier (Found : I = 47·1. $C_5H_8O_2N_3I$ requires I = 47·2 per cent.).

This salt (6·5 grams) was heated under 15—20 mm. pressure over a free flame until distillation began, and the distillate and residue were combined and crystallised from water, when 2·85 grams of pure 4-nitro-1-methylglyoxaline were obtained (93 per cent. of the theoretical). The mother-liquors left on evaporation 0·1 gram of slightly viscous residue, which was extracted with ether, when a trace dissolved. This gave with alcoholic picric acid a sparingly soluble picrate in quantity insufficient for a melting-point determination.

Methylation of 4-*Phenylglyoxaline.*—Seven grams of 4-phenylglyoxaline were mixed with 4·6 c.c. of methyl sulphate, cooled with water, when a vigorous reaction took place. The product was heated for 20 minutes in boiling water, and combined with the products from five similar experiments, representing 42 grams of 4-phenylglyoxaline in all. The melts were dissolved in water and mixed with sodium nitrate and nitric acid, when most of the unchanged 4-phenylglyoxaline separated as nitrate, which was purified by crystallisation from water.* The bases regenerated from the mother-liquor were dissolved in alcohol and mixed with 48 grams of picric acid in 1 litre of alcohol, when 31 grams of nearly pure 4-phenyl-1-methylglyoxaline picrate separated from the hot solution. Later crops furnished another 4 grams of the same material after extraction with hot alcohol. From the picrate mother-liquors, the bases were regenerated and crystallised as nitrates, when a further quantity of 4-phenylglyoxaline nitrate separated. The bases regenerated from these mother-liquors were then again converted into the picrates in alcoholic solution, and after removal of further small quantities of the almost insoluble 4-phenyl-1-methylglyoxaline picrate gave 7·0 grams of pure

* In correction of previous statements (compare Grant and Pyman, *loc. cit.*), this salt forms colourless needles, which melt and decompose at 174° (corr.), whilst the corresponding base melts at 131·5—132·5° (corr.).

5-phenyl-1-methylglyoxaline picrate. All crops of 4-phenyl-1-methylglyoxaline picrate were combined, and the base was regenerated and crystallised as hydrobromide, the mother-liquors being worked up again through the picrates. There were thus obtained in a pure state 4-phenylglyoxaline (as nitrate), 4-phenyl-1-methylglyoxaline (as hydrobromide and picrate), and 5-phenyl-1-methylglyoxaline (as picrate) in yields amounting to 27·3, 29·8, and 6·2 per cent. of the theoretical respectively. Allowing for non-recoverable quaternary salt formed in the same yield as the unchanged material, the total accounted for amounts to 90·6 per cent. The ratio of 4-phenyl-1-methylglyoxaline to 5-phenyl-1-methylglyoxaline is 4·8 : 1.

4-*Phenyl*-1-*methylglyoxaline* crystallises from ether in quadrilateral, bevelled tablets, m. p. 110—111° (corr.). It is fairly readily soluble in hot water or ether, and very readily soluble in alcohol or chloroform. It is not more soluble in aqueous sodium hydroxide than in water (Found : C = 75·8; H = 6·7. $C_{10}H_{10}N_2$ requires C = 75·9; H = 6·3 per cent.).

The *hydrobromide* crystallises from water in needles which contain $1H_2O$ and melt at 178—179° (corr.) after drying at 100°. It is somewhat sparingly soluble in water, giving a feebly acid solution (Found : in air-dried salt, loss at 100° = 7·1; in dried salt, Br = 33·4. $C_{10}H_{10}N_2,HBr$ requires Br = 33·5; + $1H_2O$ requires H_2O = 7·0 per cent.). The *nitrate* melts at about 97° (corr.). It is very easily soluble in water. The *picrate* forms microscopic needles, m. p. 245° (corr.). It is almost insoluble in boiling alcohol.

5-*Phenyl*-1-*methylglyoxaline* crystallises from ether in quadrilateral plates, m. p. 96—97° (corr.). Its solubilities are similar to those of 4-phenyl-1-methylglyoxaline (Found : C = 75·8; H = 6·6. $C_{10}H_{10}N_2$ requires C = 75·9; H = 6·3 per cent.).

The *nitrate* crystallises from water in prismatic needles which melt and decompose at 176—177° (corr.) and are somewhat sparingly soluble in cold water, giving a feebly acid solution.

The *picrate* crystallises from alcohol in prismatic needles which melt at 139° (corr.) and are readily soluble in hot, but sparingly so in cold alcohol (Found : C = 49·3; H = 3·5. $C_{10}H_{10}N_2,C_6H_3O_7N_3$ requires C = 49·6; H = 3·3 per cent.).

4(*or* 5)-*Phenyl*-1 : 3-*dimethylglyoxalinium iodide* was obtained by heating methyl iodide with either 4- or 5-phenyl-1-methylglyoxaline under reflux. It forms colourless prisms, m. p. 147—148° (corr.) (Found : I = 42·1. $C_{11}H_{13}N_2I$ requires I = 42·3 per cent.).

This salt (3·0 grams) was distilled under 15—20 mm. pressure, and the distillate (some lost) mixed with alcoholic picric acid, when 2·5 grams of pure 4-phenyl-1-methylglyoxaline picrate

separated. The base regenerated from the mother-liquors amounted to 0·18 gram. It solidified and after crystallisation from ether melted at 92°, a mixture with 5-phenyl-1-methylglyoxaline melting at 94°.

Nitration of 4-*Phenyl*-1-*methylglyoxaline*.—A solution of 10 grams of the nitrate (m. p. 97°) in 20 c.c. of concentrated sulphuric acid was heated for 1 hour in boiling water. It was then diluted with water and kept, when 0·3 gram of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline, melting at 205°, separated. After adding sodium hydroxide to the filtrate, the bases were collected partly by filtration and partly by extraction with chloroform. They were separated by fractional crystallisation of their nitrates from water when there were obtained in a pure state 6·8 grams of 4-*p*-nitrophenyl-1-methylglyoxaline nitrate (56 per cent.), together with 1·9 grams of the *nitrate* of an isomeric base, presumably 4-o-*nitrophenyl*-1-*methylglyoxaline*. This salt formed flat, colourless prisms, which decomposed at 182° (corr.) and were sparingly soluble in water (Found: C = 44·8; H = 4·0. $C_{10}H_9O_2N_3,HNO_3$ requires C = 45·1; H = 3·8 per cent.).

4-p-*Nitrophenyl*-1-*methylglyoxaline* crystallises from alcohol in pale yellow prisms, m. p. 195° (corr.). It is almost insoluble in boiling water, or aqueous sodium hydroxide, sparingly soluble in alcohol or ether, but readily soluble in chloroform (Found: C = 59·0; H = 4·6. $C_{10}H_9O_2N_3$ requires C = 59·1; H = 4·4 per cent.).

The *nitrate* forms cream-coloured, woolly needles, which melt and decompose at 197° (corr.) and are sparingly soluble in cold water. The *picrate* crystallises from alcohol in microscopic needles, which melt at 258° (corr.) and are very sparingly soluble in boiling alcohol.

Nitration of 5-*Phenyl*-1-*methylglyoxaline* was similarly effected by adding the nitrate, melting at 176—177°, to sulphuric acid, and working up as in the previous case, the main product of the reaction being 5-*p*-nitrophenyl-1-methylglyoxaline, which was isolated as pure nitrate (yield 64 per cent.).

5-p-*Nitrophenyl*-1-*methylglyoxaline* crystallises from alcohol in lemon-yellow needles, m. p. 171—172° (corr.). It is sparingly soluble in boiling water or ether, fairly readily soluble in alcohol, and readily soluble in chloroform. It is not more readily soluble in aqueous sodium hydroxide than in water (Found: C = 58·9; H = 4·4. $C_{10}H_9O_2N_3$ requires C = 59·1; H = 4·4 per cent.).

The *nitrate* crystallises from water in large, colourless plates which melt and decompose at 213° (corr.) and are sparingly soluble in cold water. The *picrate* crystallises from alcohol in prismatic needles, which melt at 184° (corr.) and are sparingly soluble in hot alcohol.

Methylation of 4-p-*Nitrophenylglyoxaline*.—Twelve grams of the base and 6·4 c.c. of methyl sulphate were heated in boiling water. After a few minutes, reaction took place with slight effervescence, yielding a clear molten mass. After heating for ½ hour, the product was mixed with sodium hydroxide, and extracted with chloroform, when persistent emulsions were obtained owing to the insoluble sodium salt of the unchanged material. The chloroform residue was crystallised from alcohol, when there were obtained in a pure state 3·6 grams of 4-*p*-nitrophenyl-1-methylglyoxaline and 0·33 gram of 5-*p*-nitrophenyl-1-methylglyoxaline, these yields being 28 and 2·6 per cent., respectively. The alcoholic mother-liquors contained more than 1 gram of a mixture of the two bases, but its separation as base or salt proved very difficult, and was not completed.

The aqueous liquor, containing the sodium salt of the unchanged material in suspension, was acidified with sulphuric acid and basified with ammonia, when 3·0 grams of 4-*p*-nitrophenylglyoxaline, m. p. 225°, were recovered unchanged.

Nitration of 4- *and* 5-p-*Nitrophenyl*-1-*methylglyoxalines*.—On adding each nitrate to concentrated sulphuric acid (2 c.c. to 1 gram), heating for ½ hour in boiling water, and pouring the solution into water, the corresponding dinitro-compound separates in a pure state (yield 90 per cent.).

5-*Nitro*-4-p-*nitrophenyl*-1-*methylglyoxaline* crystallises from alcohol in minute needles having a very faint yellow colour and melting at 208—209° (corr.). It is very sparingly soluble in ether, sparingly soluble in chloroform or hot water, but fairly readily soluble in hot alcohol or acetone (Found : C = 48·3; H = 3·5. $C_{10}H_8O_4N_4$ requires C = 48·4; H = 3·2 per cent.). It is not more soluble in aqueous sodium hydroxide than in water, but dissolves in hot concentrated hydrochloric acid, yielding a solution which deposits a crystalline *hydrochloride*. This salt yields the base on treatment with water or on heating at 100° (Found : in air-dried salt, loss at 100° = 16·4. $C_{10}H_8O_4N_4,HCl,\frac{1}{2}H_2O$ requires loss of $HCl + \frac{1}{2}H_2O$ = 15·5 per cent.).

4-*Nitro*-5-p-*nitrophenyl*-1-*methylglyoxaline* crystallises from alcohol in glistening plates having a very faint yellow colour, which soften from 185° and melt at 187° (corr.). Its solubilities are similar to those of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline (Found : C = 48·3; H = 3·4. $C_{10}H_8O_4N_4$ requires C = 48·4; H = 3·2 per cent.). It yields with strong hydrochloric or nitric acid crystalline salts which give the base on treatment with water.

Methylation of 5-*Nitro*-4-p-*nitrophenylglyoxaline*.—Twenty grams of the base and 8·2 c.c. of methyl sulphate were heated for 1 hour

in boiling water. The product was mixed with 500 c.c. of 2 per cent. warm aqueous sodium hydroxide and filtered from 10·1 grams of methylated product which melted at 203—205°. After recrystallisation from acetone, 5·6 grams of the pure substance were obtained, melting at 208—209° (corr.) alone or mixed with the nitration product of 4-*p*-nitrophenyl-1-methylglyoxaline. The mother-liquor deposited further crops of the same material of slightly lower melting point, but no 4-nitro-5-*p*-nitrophenyl-1-methylglyoxaline could be isolated. The alkaline filtrate from the methylated product deposited on cooling and again after concentration crops of the well-crystallised yellow sodium salt of the unmethylated base, of which 5·65 grams were recovered on acidification. The yield of crude methylated product is thus 66 per cent., allowing for the recovered material.

Reduction of 5-*Nitro*-4-p-*nitrophenyl*-1-*methylglyoxaline.*—Five grams of the base were added to 30 grams of hydrated stannous chloride in 80 c.c. of concentrated hydrochloric acid below 10°, and the mixture was heated for ½ hour in boiling water. After keeping, the crystalline stannichloride was collected, deprived of tin by means of hydrogen sulphide, and the solution concentrated, when 3·6 grams of the diamine dihydrochloride separated in a pure state (yield 68 per cent.).

5-*Amino*-4-p-*aminophenyl*-1-*methylglyoxaline dihydrochloride* crystallises from dilute hydrochloric acid in colourless needles which are anhydrous and darken above 200°, but do not melt at 300° (Found : C = 46·0; H = 5·7; Cl = 27·3. $C_{10}H_{12}N_4,2HCl$ requires C = 46·0; H = 5·4; Cl = 27·2 per cent.). It is readily soluble in water. Aqueous solutions of the salt give with sodium hydroxide a colourless oil which soon darkens in colour, or, with ammonia, a solution of a transient indigo colour. Its behaviour towards reagents is generally similar to that of 5-amino-4-*p*-aminophenylglyoxaline (Grant and Pyman, *loc. cit.*), but the benzylidene derivative did not crystallise, and no precipitate was obtained on adding sulphuric acid to a solution of the hydrochloride. It reduces ammoniacal silver nitrate, and gives a clear magenta solution with ferric chloride.

Hydrolysis.—3·5 Grams of the diamine dihydrochloride and 35 c.c. of concentrated hydrochloric acid were heated for 3 hours at 170°. The product consisted of 2·4 grams of large, colourless prisms and a mother-liquor, M. The crystals had the properties previously recorded (Grant and Pyman, *loc. cit.*) for *p*-aminophenylaminoacetic acid dihydrochloride, and its identity was confirmed by analysis (Found : C = 40·2; H = 5·3; Cl = 29·2, 29·6. Calc., C = 40·2; H = 5·0; Cl = 29·7 per cent.), and by its conversion

into the sparingly soluble monohydrochloride. The mother-liquor M was basified and the volatile amines were distilled into hydrochloric acid. The evaporated distillate was separated by absolute alcohol into 0·5 gram of ammonium chloride and 0·7 gram of crude methylamine hydrochloride (Found : Cl = 53·2. Calc., Cl = 52·5 per cent.).

We are indebted to Mr. I. E. Balaban, M.Sc.Tech., for analysing a number of the compounds described above.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, April 26th*, 1924.]

CLXXXII.—*The Relation between the Crystal Structure and the Constitution of Carbon Compounds. Part II. Crystallography of further Simple Substitution Products of Methane.*

By ISABEL ELLIE KNAGGS.

THE following compounds, which were prepared and discussed in relation to the isomorphism of corresponding pairs by Dr. P. V. McKie (J., 1923, **123**, 2213; this vol., p. 1075), have been examined: (1) Chlorobromoacetomethylamide, $CHClBr{\cdot}CO{\cdot}NHMe$, (2) chlorobromoacetoethylamide, $CHClBr{\cdot}CO{\cdot}NHEt$, (3) dichloroacetoethylamide, $CHCl_2{\cdot}CO{\cdot}NHEt$, (4) dichloroacetomethylanilide, $CHCl_2{\cdot}CO{\cdot}NMePh$, (5) dichloroacetoethylanilide, $CHCl_2{\cdot}CO{\cdot}NEtPh$.

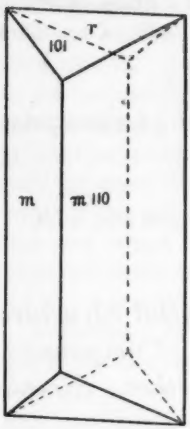
The first of these compounds, crystallising in the orthorhombic system, Evans's II Bc (holohedral) class, stands by itself. The others crystallise in the monoclinic system, Evans's II Uc (holohedral) class. As might be expected, compounds (2) and (3) are isomorphous and the isomorphism is of an extreme closeness. There is a close similarity in the ratio of the axes a and b for the three compounds (1), (2), and (3), and the angle β, which is necessarily 90° in (1), is not far removed from 90° in (2) and (3); but the ratio of the axes c and b is considerably smaller for the compound (1) than for the other two compounds (see pp. 1442, 1443).

This difference in crystal structure provides a reasonable explanation of the abnormal behaviour of the fusion mixtures of the dichloro- and chlorobromo-acetomethylamides observed by Dr. McKie (*loc. cit.*, p. 2217).

The acetoanilide compounds (4) and (5) are clearly isomorphous, although the relationship is not so close as in the case of compounds (2) and (3).

The lack of molecular symmetry of these compounds appears to find expression in the fairly low degree of symmetry shown by the crystals. In view of the recent advances in the application of the *X*-ray methods to the determination of the molecular and crystal symmetry of aliphatic compounds, it is not thought profitable at this stage to discuss further the probable significance of the experimental results given below. It is hoped, however, to continue this investigation with the aid of *X*-rays and in the light of the further evidence which they afford.

FIG. 1.



EXPERIMENTAL.

(1) *Chlorobromoacetomethylamide* (Fig. 1).

Crystal system : orthorhombic. Class : holohedral. Axial ratio : $a : b : c = 1{\cdot}094 : 1 : 0{\cdot}613$. Forms observed : m {110}, r {101}.

Angle measured :

	No. of measurements.	Limits.	Mean obs.	Calc.
$mm = (110) : (1\bar{1}0)$	8	94° 44′—95° 38½′	95° 11½′	95° 8′
$rr = (101) : (\bar{1}01)$	5	58 13½—58° 50	58 33	*
$mr = (110) : (101)$	10	70 26 —70 59	70 44	*

Habit : simple prismatic, terminated at either end of the "*c*" axis by a pair of small domal planes. The crystals are colourless, extremely small, and somewhat fibrous.

(2) *Chlorobromoacetoethylamide.*

Crystal system : monoclinic. Class : holohedral. Axial ratio : $a : b : c = 1{\cdot}092 : 1 : ?$. Axial angle : $\beta = 88° 48'$. Forms observed : $A = \{110\}$, $C = \{001\}$, $m = \{110\}$, $r = \{101\}$, $s = \{\bar{1}01\}$.

Angle measured :

	No. of measurements.	Limits.	Mean obs.	Calc.
$Ac = (100) : (001)$	7	88° 44½′—88° 51½′	88° 48′	*
$Am = (100) : (110)$	10	47 21 —47 39½	47 30	*
$Cm = (001) : (110)$	7	89 3½ —89 36	89 17	89° 11′

It has not been found possible to obtain sufficiently consistent measurements of the angles from *A*, *m*, or *C* on to *r* or *s* faces to allow of the determination of the ratio of the axis *c* to *b*. The measurements obtained indicate, however, that this ratio is probably close to the corresponding ratio found for the isomorphous dichloroacetoethylamide.

Habit : most of the crystals are flat, tabular, parallel to *C* {001} and resemble in appearance the crystals of dichloroacetoethylamide

(Fig. 2). Others are of similar habit to the two anilide compounds (4) and (5) (Fig. 3), being prismatic by elongation parallel to the "*b*" axis. The crystals are colourless and cloudy from decomposition. They readily decompose on exposure to air. It was only possible, therefore, to obtain measurements of the crystals within a short time of their removal from the crystallising dishes.

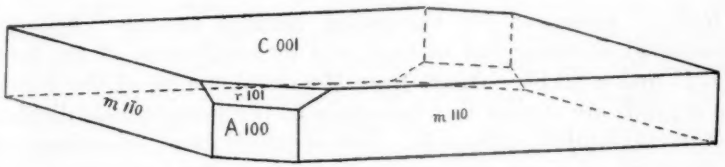
(3) *Dichloroacetoethylamide* (Fig. 2).

Crystal system: monoclinic. Class: holohedral. Axial ratio: $a : b : c = 1{\cdot}091 : 1 : 0{\cdot}783$. Axial angle: $\beta = 88° 39'$. Forms observed: $A = \{100\}$, $C = \{001\}$, $m = \{110\}$, $r = \{101\}$.

Angle measured:

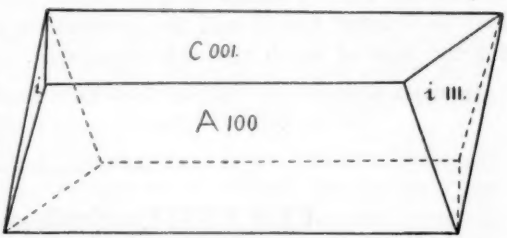
	No. of measurements.	Limits.	Mean obs.	Calc.
$Ac = (100) : (001)$	4	88° 34½′—88° 42½′	88° 39′	*
$Ar = (100) : (101)$	3	53 21 —53 37½	53 27	*
$rC = (101) : (001)$	3	34 59½ —35 30	35 14	35° 12′
$Am = (100) : (110)$	7	47 26 —47 32	47 29	*
$Cm = (001) : (110)$	6	89 8½ —89 13	89 10	89 5½

FIG. 2.



Habit: The crystals are all flat, tabular, parallel to *C* {001} (Fig. 2). Like the isomorphous chlorobromo-compound, they readily decompose in air.

FIG. 3.



(4) *Dichloroacetomethylanilide* (Fig. 3).

Crystal system: monoclinic. Class: holohedral. Axial ratio: $a : b : c = 3{\cdot}514 : 1 : 2{\cdot}949$. Axial angle: $\beta = 73° 16'$. Forms observed: $A = \{100\}$, $C = \{001\}$, $S = \{\bar{1}01\}$, $i = \{111\}$.

Angle measured:

	No. of measurements.	Limits.	Mean obs.	Calc.
$AC = (100) : (001)$	5	73° 8½′—73° 23½′	73° 16′	*
$SA = (\bar{1}01) : (\bar{1}00)$	5	59 59 —60 1	60 0	60° 2′
$Ci = (001) : (111)$	5	67 2½ —67 14	67 6	*
$Ai = (100) : (111)$	5	69 17 —69 21½	69 19	*
$ii = (111) : (\bar{1}1\bar{1})$	2	55 14 —55 16½	55 15	55 15

Habit : prismatic, parallel to the "*b*" axis, terminated at either end of that axis by a pair of small, domal faces. The crystals are clear and colourless. Although they are extremely small, they are so well developed that it is possible to obtain very accurate measurements of the angles.

(5) *Dichloroacetoethylanilide.*

Crystal system : monoclinic. Class : holohedral. Axial ratio : $a : b : c = 3{\cdot}487 : 1 : 2{\cdot}918$. Axial angle : $\beta = 72° 38'$. Forms observed : $A = \{100\}$, $C = \{001\}$, $s = \{\bar{1}01\}$, $i = \{111\}$, $e = \{\bar{2}11\}$.

Angle measured :

	No. of measurements.	Limits.	Mean obs.	Calc.
AC = (100) : (001)	4	72° 35′ —72° 43½′	72° 38′	*
Cs = (001) : ($\bar{1}$01)	6	46 42 —46 54	46 47	*
Ci = (001) : (111)	8	66 33½ —66 48	66 40	*
Ai = (100) : (111)	4	68 55½ —69 7	69 0½	68° 55′
ie = (121) : ($\bar{2}$11)	3	45 57 —46 3	45 59	46 7
si = (101) : (111)	5	84 49 —85 8	84 59½	85 1
Ce = (001) : ($\bar{2}$11)	5	81 5 —81 14½	81 9	81 8
Se = ($\bar{1}$01) : ($\bar{2}$11)	4	62 18 —62 29½	62 23	62 22
ie = (121) : (21$\bar{1}$)	4	34 45 —34 56	34 51½	34 53½

Habit : prismatic by elongation parallel to the "*b*" axis, terminated at either end of that axis by small faces of the forms i {111} and e {$\bar{2}$11}. Apart from the development of the form e, the crystals are similar in appearance to the isomorphous dichloroacetomethylanilide (Fig. 3). The crystals are colourless and transparent, of a fair size, and moderately well developed.

My thanks are again due to Dr. J. W. Evans and Prof. C. K. Ingold for their continued helpful interest. I am indebted also to Dr. McKie for her kindness in providing the material for the work and to Colonel Lyons and the authorities of the Science Museum for the loan of much valuable apparatus.

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SOUTH KENSINGTON. [*Received, March 13th*, 1924.]

CLXXXIII.—*Quebrachamine.*

By ELLEN FIELD.

QUEBRACHO bark was first extensively investigated by Hesse (*Annalen*, 1882, **211**, 249), who claimed to have isolated from it no fewer than six alkaloids, namely, quebrachine, aspidospermine, aspidospermatine, aspidosamine, hypoquebrachine, and quebrachamine. Of these, hypoquebrachine and aspidosamine are possibly only amorphous mixtures of the other alkaloids or of their decom-

position products (compare Ewins, J., 1914, **105**, 2738), whilst the presence of aspidospermatine does not appear to have been further confirmed. Aspidospermine, the chief alkaloid in the bark, had been isolated by Fraude (*Ber.*, 1878, **11**, 2189) prior to Hesse's investigation, and its occurrence was subsequently confirmed by Ewins (*loc. cit.*). The last-named author further confirmed the presence of quebrachine in the bark and at the same time claimed to have isolated two new alkaloids. One of these was stated to melt at 149—150°, and it appears probable that this is identical with quebrachamine, which has been found in the present investigation to melt at 147° instead of at 142° as stated by Hesse.

Apart from quebrachamine, the elementary composition of which has not hitherto been determined, there are thus two chemically well-defined alkaloids present in quebracho bark—quebrachine (yohimbine) with the molecular formula $C_{21}H_{26}O_3N_2$, and aspidospermine, with $C_{22}H_{30}O_2N_2$. Since quebrachamine is now prepared commercially, presumably as a by-product in the manufacture of aspidospermine, a supply of the pure alkaloid has become available. It was therefore decided to commence an investigation of the constitution of this base, especially as it was hoped that some relationship would be found between it, quebrachine, and aspidospermine, such as exists between the alkaloids of cinchona bark. The possibility of such a relationship is certainly suggested by the physiological actions of the three alkaloids. Cow (*J. Pharm. Exp. Ther.*, 1913—14, **5**, 341), who has investigated this side of the subject, finds that their actions are similar and differ only in intensity.

Quebrachamine is lævorotatory, has the molecular formula $C_{19}H_{26}N_2$, and is thus one of the few crystalline alkaloids which contain no oxygen. It is feebly basic, forming well-defined, crystalline salts only with dibasic acids such as sulphuric and oxalic acids. From its behaviour towards methyl iodide and methyl sulphate, it appears to be a monoacid tertiary base.

The nature of the second nitrogen atom has not yet been definitely ascertained, although the absence of *N*-methyl groups from the molecule, together with its behaviour towards nitrous acid, suggests that it may be present in the form of an imino-group; attempts to prepare phenylcarbamido- and acetyl derivatives, however, have been unsuccessful. The colour reactions which quebrachine gives with Ehrlich's reagent and the brilliant scarlet colour of the picrate suggest that it contains an indole grouping; this is in harmony with the presence of a non-basic imino-group and of a benzene ring. The existence of the latter is indicated by the formation of picric acid when the alkaloid is oxidised with nitric acid. The high

hydrogen content precludes the presence of more than one benzene ring.

A comparison of the molecular formulæ of quebrachamine and aspidospermine, taking into account certain groups which are known to be present in the latter, reveals a striking resemblance between the compositions of the two alkaloids. Aspidospermine, $C_{22}H_{30}O_2N_2$, has been shown by Ewins (*loc. cit.*) to contain a methoxyl and an *N*-acetyl group; the hydrolytic removal of these groups yields a base, aspidosine, with the composition $C_{19}H_{26}ON_2$. The latter is a phenolic substance and hence can be regarded as derived from a parent base, $C_{19}H_{26}N_2$, which is identical with quebrachamine in composition. Whether this identity extends beyond that of composition cannot at present be stated, but it warrants a closer comparison of the chemical properties of the two alkaloids.

Aspidospermine and quebrachamine show many resemblances. Both are feeble bases which are unattacked by concentrated sulphuric acid in the cold and give similar colour reactions with oxidising agents. Neither contains *N*-methyl groups. Whilst aspidospermine does not form any well-defined salts, aspidosine, like quebrachamine, is a monoacidic tertiary base; it contains further an imino-group and a benzene ring, and the former is probably, and the latter certainly, also present in quebrachamine.

On the other hand, there is some evidence which renders improbable the structural identity suggested by the formulæ. Thus, quebrachamine cannot be acetylated, whilst deacetylaspidospermine is readily reconverted into aspidosine by this process. Further, whereas quebrachamine forms only a monomethiodide, both nitrogen atoms in deacetylaspidospermine undergo methylation with the formation of a dimethiodide. Finally, quebrachamine differs from aspidospermine and its derivatives in giving an indole reaction with Ehrlich's reagent.

Attempts to remove the hydroxyl group from aspidosine and thus definitely to settle this question have so far been unsuccessful, but it is hoped to obtain a decisive answer by further experiments in this direction or by means of other experiments which are in progress.

No similar relationship is apparent between quebrachamine and quebrachine (yohimbine). Yohimbine, $C_{21}H_{26}O_3N_2$, is known to contain one methyl ester grouping and one non-phenolic hydroxyl group (J., 1923, **123**, 3003). Elimination of these would yield a base, $C_{19}H_{24}N_2$. This contains two hydrogen atoms less than quebrachamine, and since both substances are saturated it is impossible for them to contain the same carbon skeleton. It is

of course possible that quebrachamine contains a side chain which in yohimbine is linked in the form of a ring, but this would be difficult to demonstrate.

EXPERIMENTAL.

Properties of Quebrachamine.—Quebrachamine, colourless, rhombohedral leaflets from benzene or absolute alcohol, m. p. 147°, $[\alpha]_D$ — 109·5° in acetone ($c = 10$), is moderately soluble in the former solvents and in ether, and readily soluble in acetone (Found : in the substance twice recrystallised from alcohol and dried at 120°, C = 80·56; H = 9·08; N = 10·49; *M*, in boiling methyl alcohol, = 291. $C_{19}H_{26}N_2$ requires C = 80·85; H = 9·22; N = 9·93 per cent.; *M* = 282).

Quebrachamine distils without appreciable decomposition under the high vacuum of a rotatory oil pump with the bath at 240—250°. The distillate solidifies to a vitreous mass which on crystallisation melts at 147° and forms the characteristic red picrate of quebrachamine.

Quebrachamine gives the following colour reactions suggesting the presence of an indole grouping : with Ehrlich's reagent a purple coloration on warming, with vanillin and hydrochloric acid a violet coloration in the cold, and with the Hopkins-Adamkiewicz reagent a blue colour in the sulphuric acid layer, whilst the aqueous layer remains colourless. Characteristic colour reactions with sulphuric acid and oxidising agents are described by Hesse (*loc. cit.*), all of which have been confirmed with the exception of that given by the first-mentioned reagent. Pure concentrated sulphuric acid dissolves quebrachamine without the development of any colour, and from the solution the alkaloid may be recovered unchanged even after prolonged standing or warming, although slight traces of oxidising agents suffice to produce the blue colour noted by Hesse.

Quebrachamine appears to be fully saturated, since it does not absorb hydrogen in presence of colloidal palladium.

When a solution of sodium nitrite was added to a solution of quebrachamine in dilute acetic acid, a green oil was precipitated. On further addition of nitrite, this slowly changed to a yellow solid, which was extracted with ether. Evaporation of the ether left a solid residue, which, however, could not be crystallised.

Salts of Quebrachamine.—The *sulphate* crystallises in colourless, radiating prisms, which are readily soluble in hot, but only sparingly soluble in cold water (Found : in air-dried material, H_2O = 8·41; in material dried at 120°, S = 8·50. $C_{19}H_{26}N_2,H_2SO_4,2H_2O$ requires H_2O = 8·65. $C_{19}H_{26}N_2,H_2SO_4$ requires S = 8·42 per cent.).

The *oxalate* crystallises from absolute alcohol in radiating clusters of colourless prisms, m. p. 217° (Found: in substance dried at 115°, C = 67·76; H (lost). $C_{19}H_{26}N_2,C_2H_2O_4$ requires C = 67·74 per cent.).

A yellow, crystalline *picrate* was precipitated on addition of aqueous or alcoholic picric acid to a hot alcoholic solution of the alkaloid. This exhibited the property of chromoisomerism, for after a few minutes' boiling the colour of the crystals was slowly transformed from yellow to red. When recrystallised from absolute alcohol, in which it was sparingly soluble, the picrate formed beautiful scarlet needles, m. p. 195—196° (Found: C = 58·74; H = 5·51. $C_{25}H_{29}O_7N_5$ requires C = 58·71; H = 5·67 per cent.).

The *methiodide* was prepared by keeping 1 gram of quebrachamine and 0·4 c.c. of methyl iodide in 10 c.c. of dry acetone in the cold for several days and then adding dry ether (yield almost quantitative). It was readily soluble in acetone or ethyl alcohol and insoluble in benzene or ether. Recrystallised from methyl alcohol, it formed cream-coloured clusters of prisms, m. p. 234° (Found: C = 56·65; H = 6·59; I = 30·13. $C_{20}H_{29}N_2I$ requires C = 56·60; H = 6·84; I = 29·95 per cent.). Attempts to methylate the second nitrogen atom in quebrachamine by boiling methyl iodide were unsuccessful, and in sealed tubes at 100° with excess of methyl iodide tarry products were obtained which could not be crystallised.

The *methosulphate* was prepared from 1 gram of quebrachamine and 2 c.c. of pure methyl sulphate; the crystalline mass obtained after 12 hours was ground up with a little benzene, filtered, washed with dry ether, and precipitated from cold methyl-alcoholic solution by dry ether, slender, colourless prisms, m. p. 235°, separating, sometimes in radiating clusters. It was moderately soluble in water and very readily soluble in ethyl alcohol (Found: S = 7·99. $C_{21}H_{32}O_4N_2S$ requires S = 7·83 per cent.).

Action of Bromine on Quebrachamine.—When 1·35 grams of quebrachamine, dissolved in 20 c.c. of 80 per cent. acetic acid, were slowly treated with 5 c.c. of a 12 per cent. solution of bromine in acetic acid (10 atom.) a yellow precipitate, which at first redissolved, formed, and towards the end of the reaction, a permanent viscous precipitate, a slight excess of bromine remaining. After 1 hour, a further crystalline precipitate was deposited and the original viscous precipitate hardened to a solid. Addition of an equal volume of water and standing over-night produced a further small quantity of precipitate, the total yield of crude product being 3·7 grams.

The compound was obviously a perbromide and was somewhat

unstable, decomposing on boiling with water or other solvents. It could, however, be crystallised by suspending it in glacial acetic acid (in which it was only very sparingly soluble), to which a trace of bromine had been added, heating for a short time at 80°, and decanting the clear solution; the process was repeated with the residue. On cooling the filtrate, the perbromide crystallised in orange, radiating prisms, m. p. 160° (decomp.) (Found : in the substance dried in a vacuum, C = 30·26; H = 3·24; Br = 62·7. $C_{19}H_{24}N_2Br_6$ requires C = 30·00; H = 3·15; Br = 63·16 per cent.). The method used so successfully by Pinner (*Ber.*, 1892, **25**, 2816) in the case of nicotine to determine the number of perbromide groups present, proved inapplicable here, owing to the formation of an insoluble periodide, which vitiated the end-point of the titration. The results, therefore, are not recorded in detail, although the values obtained agreed approximately with the presence of one perbromide group. This received confirmation from the composition of a product which was obtained from the perbromide in the manner described below and contained three bromine atoms.

On prolonged boiling with water, the perbromide (1 gram) lost bromine, and a white precipitate formed which increased in amount and became finely crystalline on cooling (yield 0·6 gram). This compound, which was exceedingly sparingly soluble in water, alkalis, and in most organic solvents, was rather more soluble in methyl than in ethyl alcohol, and was best recrystallised from the former, or from ethyl acetate, separating in colourless rosettes of needles which did not melt at 290° (Found : C = 42·31; H = 4·53; Br = 44·80. $C_{19}H_{25}ON_2Br_3$ requires C = 42·46; H = 4·65; Br = 44·69. $C_{19}H_{23}ON_2Br_3$ requires C = 42·61; H = 4·32; Br = 44·86 per cent.). This compound is unchanged by sodium hydroxide and therefore is not a hydrobromide, and since, further, quebrachamine can be regarded as fully saturated, it follows that the three bromine atoms must have entered the molecule by substitution. Hence the second formula is the more probable. The nature of the oxygen atom is undetermined. The bromo-compound is reduced by sodium in boiling alcoholic solution; not only are three bromine atoms removed, but the oxygen also is eliminated with the regeneration of quebrachamine.

Oxidation of Quebrachamine.—Various oxidising agents were employed in attempts to degrade quebrachamine. With potassium permanganate in acetone solution and with chromic acid in acetic acid solution, oxidation took place readily, but in each case the product was amorphous and evidently consisted of a mixture of substances. Nitric acid, under various conditions, was also used,

but in most cases the product was amorphous and consisted of a mixture of nitro-derivatives. When, however, the alkaloid was heated with 30 per cent. nitric acid at 150° in a sealed tube, picric acid was obtained in small yield.

In conclusion, the author wishes to thank Prof. G. Barger, F.R.S., for kindly suggesting this work, and to express her indebtedness to the Earl of Moray Fund of this University for a grant in aid of the investigation.

DEPARTMENT OF MEDICAL CHEMISTRY,
UNIVERSITY OF EDINBURGH. [*Received, March 27th*, 1924.]

CLXXXIV.—*The Action of Thionyl Chloride on Hydroxyanthraquinones. Part I. Thionylalizarin.*

By ALBERT GREEN.

THIONYLALIZARIN, a crystalline substance obtained by the interaction of alizarin and boiling thionyl chloride, is less stable than the analogous sulphate of alizarin bordeaux (Schmidt, *J. pr. Chem.*, 1891, [ii], **43**, 239; Gattermann, *ibid.*, p. 248). It is stable in a dry atmosphere, but moisture converts it completely into alizarin. The colours of its solutions in aqueous sodium hydroxide and in concentrated sulphuric acid are the same as those of alizarin, and, in the latter case, this compound is precipitated on addition of water.

Thionylalizarin reacts with boiling glacial acetic acid and with boiling acetic anhydride to give 2-acetylalizarin and diacetylalizarin, respectively. The former reaction is another example of the influence of the carbonyl groups in stabilising a hydroxyl group in the 1-position of the anthraquinone molecule (compare Perkin, J., 1899, **75**, 447; Dimroth, Friedmann, and Kämmerer, *Ber.*, 1920, **53**, 481).

EXPERIMENTAL.

Thionylalizarin, $C_{14}H_6O_2<^{O}_{O}>SO$.—No appreciable reaction occurred when alizarin and thionyl chloride were heated for 24 hours in dry nitrobenzene at 100°.

A mixture of 20 grams of dry alizarin and 200 c.c. of pure thionyl chloride was heated under reflux on the water-bath for 3 hours (in other experiments, for 18 hours), hydrogen chloride being evolved after 15 minutes, the dark red solution was concentrated to 60 c.c., cooled in absence of moisture, and rapidly filtered after 2 hours; the crystals were quickly washed with dry benzene and with dry ether, the last traces of ether were removed in a vacuum, and the

product (23 grams) was recrystallised from absolute ether or dry benzene, *thionylalizarin* separating in primrose-yellow crystals, m. p. 171—172°. When kept in a sealed tube for a few hours, these became orange-yellow, but the melting point and sulphur content were unchanged [Found: C = 58·7; H = 2·2; S = (*a*) 11·1, (*b*) 11·6, (*c*) 11·0; *M*, in freezing naphthalene, = 283. $C_{14}H_6O_5S$ requires C = 58·7; H = 2·1; S = 11·2 per cent.; *M* = 286. The sulphur was estimated by Carius's method (*a*), and iodometrically as sulphur dioxide, produced by (*b*) cold caustic soda solution and (*c*) boiling glacial acetic acid].

Monoacetylalizarin.—Thionylalizarin (5 grams) was boiled with 75 c.c. of glacial acetic acid until evolution of sulphur dioxide had practically ceased (35 minutes). After 12 hours, the crystals (4·2 grams) deposited, together with a further 0·7 gram precipitated on addition of water, were recrystallised from pyridine and absolute alcohol, and monoacetylalizarin was obtained in golden-yellow crystals, melting at 201—202° alone or mixed with a specimen prepared from alizarin and acetic anhydride in pyridine solution (Found: $CH_3{\cdot}CO$ = 15·5. Calc., 15·3 per cent.).

Diacetylalizarin.—The crystals (2·6 grams deposited and 0·35 gram on dilution) obtained in a similar way from 2·7 grams of thionylalizarin and 10 c.c. of boiling acetic anhydride separated from rectified spirit in pale green needles, which sintered at 178° and melted at 185°, alone or mixed with diacetylalizarin prepared from alizarin and acetic anhydride in pyridine (Found: $CH_3{\cdot}CO$ = 26·2. Calc., 26·5 per cent.).

The author wishes to thank Professor T. Campbell James for his interest and for providing facilities which have made this work possible, and also the Research Fund Committee of the Chemical Society, a grant from whom has defrayed part of the expenses of this research.

THE EDWARD DAVIES LABORATORIES,
UNIVERSITY COLLEGE, ABERYSTWYTH. [*Received, April 5th*, 1924.]

CLXXXV.—*The Solubility of Sodium Fluoride in Hydrofluoric Acid.*

By DAVID BRET JEHU and LAWSON JOHN HUDLESTON.

THE solubility of sodium fluoride in hydrofluoric acid was investigated at 21° by Ditte (*Compt. rend.*, 1896, **123**, 1283), but he did not determine the composition of the solid phase in equilibrium

with the saturated solutions. As this information was required for other work, a fresh study at 20° was undertaken.

Hydrofluoric acid and sodium hydroxide solution, prepared as described by Davies and Hudleston (this vol., p. 260), were mixed, in a platinum dish, so as to give solutions each having a volume of about 100 c.c. and containing 8 grams of sodium fluoride and a different quantity of acid. The solutions and precipitates were transferred to conical flasks of pure paraffin wax fitted with wax stoppers, and these were tightly sealed and attached to the paddles of a stirrer in a thermostat kept at 20°. The temperature occasionally varied by as much as 1°, but was always maintained at 20° $\pm$ 0·2° on the day previous to the analysis. To ensure the production of equilibrium, duplicate solutions were kept in the thermostat for a fortnight and a month, respectively, before being analysed; complete agreement was always obtained.

In order to prevent cooling, and consequent deposition of solid, during filtration and at the same time retain the simple construction of the wax apparatus, an unusual method was adopted. A wax cylinder (*a*), closed at the bottom and strengthened with external rings of cardboard, was immersed nearly to the brim in the thermostat and allowed to acquire its temperature. The mixture to be filtered was poured into (*a*), and a second cylinder (*b*), of slightly smaller diameter, with a perforated bottom closed with filter-paper (the edges were sealed all round with wax), which had meanwhile been kept in a beaker in the thermostat, was forced down through the liquid by the weight of a loosely fitting lid. The liquid thus filtered upwards into *b*, from which the samples for analysis were removed in wax pipettes. The further filtration to obtain the solid phase could now be carried out without regard to the filtrate. For this purpose, an ordinary filter flask was lightly waxed inside and into the neck was sealed a wax cylinder (*c*) with a perforated bottom, closed with filter-paper, which was firmly sealed with wax at the edge. The whole was placed in the thermostat so that only an inch of *c* projected above the water, communication between the atmosphere and the interior of the flask being made by rubber tubing attached to the side tube. The residue in *a* was quickly emptied into *c*, the level of the liquid never being above that of the water in the thermostat. The final filtration was hastened by blowing with air free from carbon dioxide, but even so the "solid" obtained contained about 50 per cent. of mother-liquor.

Solutions and solid phases were analysed in the same way. Mixtures of weighed portions (in duplicate) and strong sulphuric acid were cautiously evaporated to dryness in platinum crucibles, and the residues heated to dull redness to obtain the sodium content

and hence that of the sodium fluoride. The acid was estimated by titrating weighed portions (also in duplicate), in wax vessels, with pure sodium hydroxide and phenolphthalein, sufficient water being added to give clear solutions in the case of the solid phases. The water content was determined by difference. Only the mean of the results is given in the table, since the values were practically identical.

A blank test with the sulphuric acid showed that this left no weighable residue. The caustic soda was standardised with twice recrystallised succinic acid and the same indicator. The experimental accuracy is indicated by the agreement obtained with the

Grams per 100 grams of water.

	Solution.		Solid.			
No.	HF.	NaF.	HF.	NaF.	Slope.	Solid phase.
1	0·081	4·14	0·079	140·5	−68,200	NaF.
2	0·104	4·19	0·138	116·1	3,280	
3	0·135	4·23	0·154	92·95	4,719	
4	0·420	4·51	0·448	78·78	2,653	
5	0·473	4·58	3·56	84·40	25·83	NaF and NaF, HF.
6	0·473	4·59	19·57	117·4	5·91	
7	0·483	4·58	44·04	125·2	2·77	
8	0·485	4·56	5·01	82·86	17·32	
9	0·492	4·54	20·01	126·3	6·24	
10	0·496	4·50	24·87	74·92	2·99	
11	0·660	3·45	23·06	51·61	2·15	NaF, HF.
12	0·831	2·99	33·65	71·47	2·09	
13	1·16	2·46	26·41	55·73	2·11	
14	1·20	2·49	28·35	58·21	2·05	
15	1·55	2·20	29·32	60·44	2·09	
16	2·22	2·04	23·53	44·53	2·00	
17	2·50	2·00	30·54	60·32	2·08	
18	2·70	2·01	36·12	72·55	2·11	
19	4·17	1·88	32·98	62·15	2·09	
20	8·68	1·83	54·84	100·3	2·13	
21	10·28	1·79	38·84	60·32	2·05	

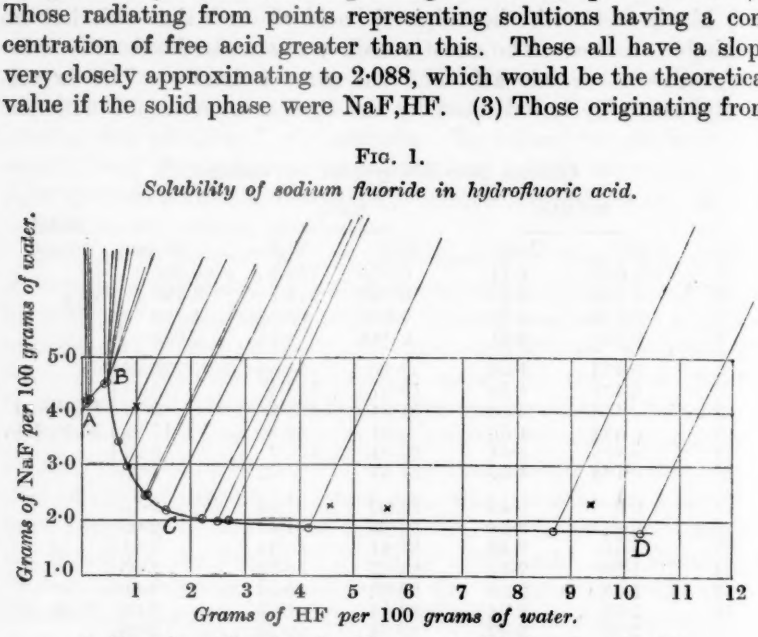
various samples of invariant solution (see table) and by the approach to the theoretical value of the "slopes" given in the penultimate column. The results are also shown graphically in Fig. 1.

Owing to the small solubility of sodium fluoride, the ordinary triangular diagram is not a suitable method of representation. We have therefore used rectangular co-ordinates, representing grams of sodium fluoride and hydrogen fluoride, respectively, per 100 grams of water. In this form also, it is true that a mixture of two phases must have a composition represented by some point on the straight line joining the points representing the composition of each. Consequently, the lines joining the points representing the saturated solution and the moist solid, when prolonged, should pass through

the point representing the solid phase. This will be at infinity if the solid is anhydrous, but the slope of the line will be given by the ratio of the weights of sodium fluoride and hydrogen fluoride in the solid phase. From Fig. 1 it is clear that there are three groups of such lines. (1) Those radiating from points representing solutions containing less than 0·48 gram of free acid per 100 grams of water. These are practically vertical, corresponding to the solid phase NaF. (2) Those radiating from points representing solutions having a concentration of free acid greater than this. These all have a slope very closely approximating to 2·088, which would be the theoretical value if the solid phase were NaF,HF. (3) Those originating from

FIG. 1.

Solubility of sodium fluoride in hydrofluoric acid.



⊙ *Experimental points for* 20°. × *Ditte's values for* 21°.

the point *B* (invariant solution), with a slope between these values indicating a mixture of the two solid phases. It is inconvenient to plot the composition of the moist solids in the diagram, as it would necessitate the use of a much smaller scale, and therefore only the slopes of the lines, calculated directly from the analytical data, are given.

The curve *ABCD* is the saturation curve for sodium fluoride in hydrofluoric acid, but the solid phase in equilibrium with the solutions represented by points on the line *BCD* is NaF,HF. The form of the curve is qualitatively explained by the formation of the complex ion HF_2' in the reaction $F' + HF = HF_2'$, which has already been established from conductivity data (Pick, Nernst's "Festschrift," 1912, 360) and transference numbers (Davies and Hudleston, *loc. cit.*). In neutral solution, the solubility of sodium

fluoride is determined by the solubility product of the sodium and fluorine ions. The addition of the weak hydrofluoric acid introduces but little common ion from its own dissociation and removes much of that produced from the salt by the formation of the complex ion as given above. The concentration of sodium ion therefore increases with increasing acid concentration until the solubility product of the ions $Na^{\bullet}$ and HF_2' is reached in the solution represented by the point *B*. The further addition of acid, by converting more F' into HF_2', rapidly increases the concentration of this ion, so that of the sodium ion decreases with corresponding rapidity as the acid concentration is increased. At about the point *C*, the proportion of fluorine ion (originating mainly from the salt) is so small that further addition of acid can produce very little more complex ion by combination, nor does it introduce much from itself, since it is not greatly dissociated (compare the conductivity); consequently the concentration of sodium ion falls off but slowly thereafter with increasing acid concentration. It will not be possible to give a quantitative explanation until the activity coefficients of the substances concerned are known for these comparatively high concentrations. As a very crude approximation, we may set $K = [HF_2']/[HF][F'] = 4{\cdot}7$ as found by Davies and Hudleston (for 25°), suppose the salt to be completely ionised and the acid quite undissociated, when $[Na^{\bullet}] = [HF_2'] + [F']$, solve for $[HF_2']$, and calculate $[Na^{\bullet}] \times [HF_2']$, and thus obtain a "constant" varying from 2·2 — 1·8 over the whole range *BCD*. Doubtless this approximation to a constant is due to the fact that the concentration of the salt varies only from about molar to half molar, and the activity coefficient should not change very much in this interval (*e.g.*, for sodium chloride, $\gamma = 0{\cdot}68$ and 0·63 at these concentrations. Lewis and Randall, "Thermodynamics," 1923, p. 348). This suggests that the explanation is adequate, although we lack the knowledge to make it quantitatively exact.

Ditte's results at 21° are shown by the crosses in Fig. 1. He failed to observe the critical part of the curve, where the nature of the solid phase in equilibrium with the solution changes. His values are almost uniformly higher than ours for the more acid solutions, perhaps because he had not secured equilibrium. Moreover, he recorded a point of minimum solubility at about 6 per cent. of acid which our results do not confirm.

For the solubility of sodium fluoride in pure water we obtain, by a slight extrapolation, 3·96 grams per 100 grams of water at 20°. In the same terms, Ditte found 4·17 at 21°, Fremy (*Ann. Chim. Phys.*, 1856, [iii], **47**, 32) 4 at 15°, whilst Mylius and Funk (*Ber.*, 1897, **30**, 1718) obtained 4·5 at 18°.

We wish to express our appreciation of the kindness of the Scottish Oil Agency, Ltd., in providing the wax from which the vessels used were made.

THE EDWARD DAVIES LABORATORIES,
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CLXXXVI.—*The Additive Formation of Four-membered Rings. Part V. The Formation of Stable Dimethylene-1 : 2-oxaimines from Ethylenes and Nitroso-compounds, with Special Reference to the Direction of the Addition.*

By CHRISTOPHER KELK INGOLD and STANLEY DOUGLAS WEAVER.

IN continuation of previous papers (J., 1922, **121**, 2793; 1923, **123**, 2745; this vol., pp. 87, 123) in which compounds have been described containing the rings (I), (II), and (III), this paper deals with derivatives of the ring (IV), which have been produced, like the previous compounds, by the additive union of unsaturated molecules—in the present case an ethylene derivative and a nitroso-compound (C:C + N:O).

(I.) (II.) (III.) (IV.)

*Stability of the Dimethyleneoxaimine * Ring* (IV).

These studies have shown that the conditions of substitution favouring the formation and stability of heterocyclic four-membered rings are similar to those applicable to homocyclic rings. Thus in the dimethyleneoxaimine series (IV) it is desirable to have a bulky *gem*-grouping attached to one of the ring-bound carbon atoms to ensure the production of a stable compound.

It follows that a *gem*-disubstituted ethylene, such as (V) or (VI), is best employed as one of the addenda for the formation of these rings. The effect of the absence of a *gem*-grouping is illustrated on p. 1459.

(V.) $CH_2{:}C(CO_2Et)_2$ $CH_2{:}C(C_6H_5)_2$ (VI.)

Many of the four-membered rings previously studied were unstable, and one of the objects of these investigations was the discovery of conditions in which stable four-membered rings could arise. The

* The nomenclature is that proposed in a previous paper (Ingold, this vol., p. 87).

dimethyleneoxaimines now described are amongst the most stable four-membered heterocyclic compounds hitherto produced.

Direction of the Addition and the Theory of Alternate Polarities.

In Part III it was pointed out that the direction of an additive ring-synthesis forms a good test of the polarity theory, especially that of double bonds (Lowry, J., 1923, **123**, 822; also *Chem. and Ind.*), and that, for the cases described, the theory was in conflict with the facts, $\overset{-}{N}:\overset{+}{C}$ and $\overset{-}{O}:\overset{+}{N}$ uniting to produce $\begin{matrix}N-C\\ |\ \ |\\ O-N\end{matrix}$ rather than $\begin{matrix}N-C\\ |\ \ |\\ N-O\end{matrix}$.

It is true that bulky groups were attached to the nitrogen atoms in those cases, and it was suggested to us that the results could be explained on the ground that a tendency to avoid congestion of the bulky groups would determine the structure produced. The opportunity has now been taken to test this suggestion.

For this purpose, we have synthesised, not only dimethyleneoxaimines with their bulky groups separated, but also ones with their large groups in adjacent positions, and in either case have found that the direction of the addition is contrary to the indications of the polar theory.

Thus the ethylene derivative (V) readily combines with aromatic nitroso-compounds to form rings of type (VII), and not (VIII), which should be the type produced if oxygen key-atoms determine the polarities: $Ar\cdot\overset{+}{N}:\overset{-}{O}$; $\overset{+}{C}H_2:\overset{-}{C}(\overset{+}{C}O_2Et)$. The constitution of the ring follows from the thermal degradation, which leads to an ester-anilide (IX) (compare Part III), and not to formaldehyde and the anil (X), the products to be expected from a compound of formula (VIII).

(VII.) $\begin{matrix}CH_2-C(CO_2Et)_2\\ |\ \ \ \ |\\ C_6H_5\cdot N-\!\!-O\end{matrix}$ $\begin{matrix}CH_2-C(CO_2Et)_2\\ |\ \ \ \ |\\ O-\!\!-N\cdot C_6H_5\end{matrix}$ (VIII.)

$\downarrow$

$C_6H_5\cdot N{:}C{:}C(CO_2Et)_2$

$\downarrow$

(IX.) $C_6H_5\cdot NH\cdot CO\cdot CH(CO_2Et)_2$ $\qquad$ $CH_2O + \begin{matrix}C(CO_2Et)_2\\ \|\ \ \ \ \ \ \\ N\cdot C_6H_5\end{matrix}$ (X.)

A similar experiment in the keten series has been carried out by Staudinger and Jelagin (*Ber.*, 1911, **44**, 365). According to the polarity theory, diphenyl keten, $\overset{-}{O}\overset{+}{C}:\overset{-}{C}Ph_2$, should unite with nitrosobenzene to give

(XI.) $\begin{matrix}(C_6H_5)_2C-\!\!-CO\\ |\ \ \ \ \ \ \ \ |\\ C_6H_5\cdot N-\!\!-O\end{matrix}$ and not $\begin{matrix}(C_6H_5)_2C-\!\!-CO\\ |\ \ \ \ \ \ \ \ |\\ O-\!\!-N\cdot C_6H_5\end{matrix}$ (XII.)

Actually, (XII) was the main product and, moreover, the stable one, whilst (XI) was formed in traces only and showed great instability.

For the study of cases in which the polar theory predicts the formation of a compound with its bulky groups separated, it was necessary to employ an ethylene in which (using the language of the polar theory) the polarities are oppositely directed, with respect to the heavy substituent, to those in (V).

Diphenylethylene (VI) and also styrene (cf. p. 1459) fulfil this condition, possessing properties which can be represented by the polar formulae $\overset{-}{C}H_2{\cdot}\overset{+}{C}Ph_2$ and $\overset{-}{C}H_2{\cdot}\overset{+}{C}HPh$. Thus the addition of hydrogen chloride and bromide leads to compounds such as $CH_3{\cdot}CHClPh$, etc., the "positive" carbon attracting the "negative" halogen; the addition of hypoiodous acid leads to $CH_2I{\cdot}C(OH)Ph_2$ and $CH_2I{\cdot}CH(OH)Ph$, the "positive" carbon attracting the hydroxyl group; again, in nitration, the "positive" $-\overset{+}{N}O_2$ group enters at the "negative" carbon atom (ω-position).*

According to the polar theory, then, $\overset{-}{C}H_2{\cdot}\overset{+}{C}Ph$ should unite with $O{:}\overset{+}{N}Ph$ to form

(XIII.) $(C_6H_5)_2C(-O-N{\cdot}C_6H_5)-CH_2$ and not $CH_2(-O-N{\cdot}C_6H_5)-C(C_6H_5)_2$ (XIV.)

Moreover, in this case, if there is any tendency to avoid the congestion of groups, it should operate in favour of the polar theory. It is especially noteworthy, therefore, that the additive product was found to have formula (XIV), and that even traces of (XIII) could not be detected. The thermal division of (XIV) yielded benzophenoneanil and formaldehyde.

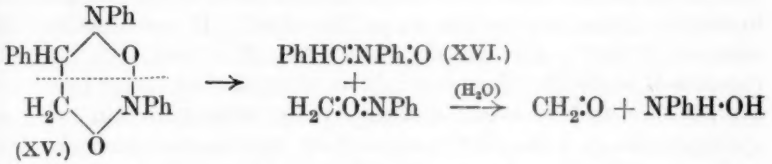
It might be contended that these results are explicable on the polarity theory if it be assumed that the usual order of the charges is reversed in the nitroso-group: $R{\cdot}\overset{-}{N}{:}\overset{+}{O}$. Such a conception, however, neglects all the analogies between the reactions of the nitroso-group [*e. g.*, with NH_2Ph, $CH_2(CN)Ph$, etc.] and those of the carbonyl group, invariably designated $\overset{+}{C}{:}\overset{-}{O}$. Further, the device of changing the signs when circumstances seem to require it, if once admitted, could not be restricted to the nitroso-group (there

* Robinson has explained (*Ann. Rep.*, 1923, pp. 91—92) Ziegler and Thielmann's results on the fission of aryl ethers (*Ber.*, 1923, **56**, 1740) by the hypothesis that the phenyl group is "key-positive." In the examples given above, it appears as "key-negative," a circumstance which a less flexible theory might find it difficult to accommodate.

is evidence that it would have to be applied to C:S), and such a loose procedure would weaken the theory, even more, perhaps, than the adverse facts described in this paper.

Irregular Reactions in Cases of Deficient Substitution.

Reference has been made to the irregular reactions which may take place when the *gem*-group required to facilitate the formation of the four-membered ring is absent. Many experiments have been made on this point, but it will suffice here to contrast the reactions of diphenylethylene and of styrene with aromatic nitroso-compounds. Apparently, in the reaction with styrene, as in other cases of insufficient substitution, the product is a six-membered ring (XV), which, in the present instance, breaks down in the manner shown, yielding *N*-phenylbenzaldoxime, formaldehyde, and phenylhydroxylamine :



EXPERIMENTAL.

(A.) *Ring-additions with Ethyl Methylenemalonate.*

The freshly distilled ester was used for all the experiments described below.

Addition to Nitrosobenzene : Formation of Ethyl 2-Phenyldimethylene-1 : 2-oxaimine-4 : 4-dicarboxylate (VII).—Nitrosobenzene (3 grams, *i. e.*, about 1·5 times the theoretical quantity) was dissolved in the minimal quantity of chloroform, and 3 grams of ethyl methylenemalonate were added. A vigorous reaction occurred and was complete after a few minutes, during which much heat was developed, the solution boiling spontaneously. The solvent was removed in a vacuum, and the residue rubbed with a little ether, drained, and crystallised first from ether and finally from aqueous alcohol, from which it separated in long, colourless needles, m. p. 98—100°, the yield being almost theoretical. The compound exhibits no tendency to salt formation either with strong acids or alkalis; it gives no colour with ferric chloride, no copper salt, and is oxidised by alkaline potassium permanganate only with difficulty (Found : C = 60·01; H = 6·05; N = 5·10. $C_{14}H_{17}O_5N$ requires C = 60·22; H = 6·09; N = 5·02 per cent.).

Thermal Decomposition of the Dimethyleneoxaimine : Formation of Dicarbethoxyacetanilide (IX), etc.—When heated alone at 180°.

or for a long time at 100° the dimethyleneoxaimine yields dicarbethoxyacetanilide. At higher temperatures, this compound itself breaks down into ethyl malonate and phenylcarbimide, which, to a considerable extent, combines with the unchanged dicarbethoxy-compound, yielding 6-anilino-2 : 4-diketo-3-phenyl-2 : 4-dihydro-1 : 3-oxazine (XVII).

$$\text{(IX.)} \longrightarrow \text{NPh:CO} + \text{CH}_2(\text{CO}_2\text{Et})_2.$$

$$\underset{\text{(enolic form of IX.)}}{\text{NHPh}\cdot\text{C}(\text{OH}):\text{C}(\text{CO}_2\text{Et})_2} + \text{NPh:CO} \longrightarrow \underset{\text{O}\cdot\text{CO}\cdot\text{NPh}}{\text{NHPh}\cdot\text{C}:\text{CH}\cdot\text{CO}} \quad \text{(XVII.)}$$

Dicarbethoxyacetanilide (IX) was best obtained as follows: The dimethyleneoxaimine was heated in an open tube at about 100° for 4 hours. After cooling, the product was mixed with ether, and the sparingly soluble crystalline material collected and crystallised twice from 95 per cent. ethyl alcohol, from which it separated in slender, colourless needles, m. p. 128—129°. It was identified by analysis (Found: C = 59·96; H = 6·20; N = 5·14. $C_{14}H_{17}O_5N$ requires C = 60·22; H = 6·09; N = 5·02 per cent.), and by direct comparison and a mixed-melting point determination with a specimen (m. p. 128—130°) prepared by the condensation of ethyl malonate with phenylcarbimide (Michael, *J. pr. Chem.*, 1887, [ii], **35**, 451) (Found: C = 60·34; H = 6·16 per cent.).

6-*Anilino*-2 : 4-*diketo*-3-*phenyl*-2 : 4-*dihydro*-1 : 3-*oxazine* (XVII). —This is best obtained by heating dicarbethoxyacetanilide for a few minutes at 240—250° in an open tube. The product solidifies while still hot and smells strongly of phenylcarbimide, the presence of which can readily be proved by adding aniline to the filtered ethereal extract (in which the crystalline substance is insoluble) of the product, when diphenylcarbamide immediately separates. The crystalline substance is sparingly soluble in all the usual solvents, but separates from a large volume of boiling ethyl alcohol in colourless, slender needles, m. p. 293—294° (Found: C = 68·28; H = 4·23; N = 10·02. $C_{16}H_{12}O_3N_2$ requires C = 68·57; H = 4·29; N = 10·00 per cent.).

Addition to p-*Chloronitrosobenzene: Formation of Ethyl* 2-p-*Chlorophenyldimethylene*-1 : 2-*oxaimine*-4 : 4-*dicarboxylate*. — One gram of ethyl methylenemalonate was added to an equal weight (1·2 times the theoretical quantity) of *p*-chloronitrosobenzene dissolved in the minimal amount of hot chloroform. The reaction proceeded with evolution of heat and was complete in 10 minutes, after which the chloroform was evaporated and the residue rubbed with dry ether and crystallised from 95 per cent. alcohol. The product formed colourless needles, m. p. 122—123° (Found: C =

53·35; H = 5·03; N = 4·50. $C_{14}H_{16}O_5NCl$ requires C = 53·68; H = 5·11; N = 4·47 per cent.).

Addition to p-*Bromonitrosobenzene: Formation of Ethyl* 2-p-*Bromophenyldimethylene*-1 : 2-*oxaimine*-4 : 4-*dicarboxylate.*—The ethyl methylenemalonate and *p*-bromonitrosobenzene (1·2 times the theoretical) were allowed to react in boiling chloroform as above described, and the product was crystallised three times from ether, from which it separated in long, colourless needles, m. p. 132—133° (Found: C = 46·95; H = 4·43; N = 4·25. $C_{14}H_{16}O_5NBr$ requires C = 46·91; H = 4·47; N = 3·91 per cent.).

(B.) *Ring-addition with* as-*Diphenylethylene.*

Addition to Nitrosobenzene: Formation of 2 : 3 : 3-*Triphenyldimethylene*-1 : 2-*oxaimine* (XIV).—The hydrocarbon (3 grams) was added to a concentrated chloroform solution of 3 grams (1·7 times the theoretical) of nitrosobenzene, and the solution kept over-night. The crystals were then collected, combined with a further quantity obtained from the mother-liquors by evaporation and treatment with ether, and crystallised from alcohol, from which nearly colourless needles separated, m. p. 218—220°. The substance was not an aldehyde and was neither basic nor acid and gave no iron or copper salt, and its stability towards permanganate and general properties (except thermal division) closely resembled those of the dimethyleneoxaimines described above (Found: C = 83·56; H = 5·61; N = 5·20. $C_{20}H_{17}ON$ requires C = 83·62; H = 5·92; N = 4·90 per cent.).

The ultimate residues, after long keeping, yielded a trace (0·6 gram from 90 grams of residues) of diphenylcarbamide (Found: C = 73·52; H = 5·84. Calc., C = 73·58; H = 5·66 per cent.).

Thermal Division of the Dimethyleneoxaimine into Benzophenoneanil and Formaldehyde.—This decomposition was carried out by distilling the dimethyleneoxaimine at 70 mm. pressure in an apparatus arranged so that the gaseous product could be collected as well as the liquid distillate. The formaldehyde evolved during the distillation was readily identified in the usual way. The liquid distillate, which solidified completely to a mass of yellow crystals, consisted essentially of benzophenoneanil. It was purified by evaporating a filtered solution in light petroleum (b. p. 60—80°) to dryness, and recrystallising the residue four times from ethyl alcohol. The product did not depress the m. p. (114°) of an authentic specimen of benzophenoneanil (Found: C = 88·28; H = 5·93. Calc., C = 88·72; H = 5·84 per cent.).

(C.) *Reactions with Styrene.*

Reaction of Nitrosobenzene: Formation of N-*Phenylbenzaldoxime* (XVI), *Formaldehyde* (*Formic Acid*), *and Phenylhydroxylamine* (p-*Aminophenol*).—Equimolecular quantities of styrene and nitrosobenzene yielded no detectable quantity of a dimethyleneoxaimine when allowed to react in ether, chloroform, or alcohol, either in the cold or the boiling solvent. *N*-Phenylbenzaldoxime was, however, readily isolated in all cases. It crystallised from ether in long, slender needles, m. p. 112—113°, and did not depress the melting point of an authentic specimen prepared from benzaldehyde and phenylhydroxylamine (Bamberger, *Ber.*, 1894, **27**, 1556) (Found: C = 78·89; H = 5·58; N = 7·24. Calc., C = 78·63; H = 5·58; N = 7·11 per cent.).

The mother-liquors from this substance, on distillation, yielded only unchanged styrene and complex decomposition products; but after boiling for 1 hour with dilute sulphuric acid formic acid was found to be present and could be separated by distillation in steam and identified in the usual way. The formaldehyde which should have been produced could not be detected, and must be supposed to have oxidised completely to formic acid under the conditions employed. The residue from the steam-distillation contained *p*-aminophenol, evidently derived by the action of the sulphuric acid on phenylhydroxylamine.

Reaction with p-*Chloronitrosobenzene: Formation of* N-p-*Chlorophenylbenzaldoxime.*—The nitroso-compound (4·2 grams) was dissolved in the minimal quantity of chloroform, and the solution mixed with an equivalent (3·1 grams) of styrene, and kept for 20 hours at 5°, after which the green colour had given place to a deep red. The solvent was evaporated in a vacuum, and the solid residue crystallised repeatedly from a mixture of chloroform and ether, from which the pure oxime separated in fern-like clusters of needles, if crystallised slowly, or glistening leaflets if crystallised rapidly, m. p. 172—173° (Found: C = 67·16; H = 4·45; N = 5·97; Cl = 15·66. $C_{13}H_{10}ONCl$ requires C = 67·39; H = 4·32; N = 6·05; Cl = 15·32 per cent.).

We desire to take this opportunity to thank the Royal and Chemical Societies for defraying a considerable portion of the cost of this research.

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SOUTH KENSINGTON, S.W. 7. [*Received, April 29th*, 1924.]

CLXXXVII.—*Action of Diazo-salts on Methanesulphonamide.*

By PAVITRA KUMAR DUTT.

IT has been shown by Dutt, Whitehead, and Wormall (J., 1921, **119**, 2088) that the action of diazo-salts on aromatic sulphonamides can be expressed by the equations :

I. $R{\cdot}SO_2{\cdot}NH_2 + R'{\cdot}N{:}NX \rightarrow R{\cdot}SO_2{\cdot}NH{\cdot}N{:}NR' \rightarrow R{\cdot}SO_2H + R'N_3$.

II. $R{\cdot}SO_2H + R'{\cdot}N{:}NX \longrightarrow R{\cdot}SO_2{\cdot}N{:}NR' + HX$.

It is now shown that the same reactions take place with extreme ease in the case of an aliphatic sulphonamide, such as methanesulphonamide. With benzenediazonium chloride, it is possible to distinguish the two stages of the reaction, whereas with *p*-toluenediazonium chloride the decomposition of the diazoamine is so rapid that the diazosulphinate separates out before the full quantity of the diazo-salt (according to equation I) has been added. The action of benzenediazonium chloride on toluene-ω-sulphonamide also has been examined, but only phenylazoimide could be isolated from the tarry product. The stability of these diazoamines, therefore, seems to depend, not on the mass of the substituent groups, but on some other influence at present unknown.

EXPERIMENTAL.

Preparation of Methanesulphonamide.—The following method seems more satisfactory than the existing ones (Kolbe, *Annalen*, 1845, **54**, 174; Carius, *ibid.*, 1860, **114**, 142; Collman, *ibid.*, 1868, **148**, 105; Gowan, *J. pr. Chem.*, 1884, [ii], **30**, 281). Methyl sulphate (100 grams) is slowly dropped during 1 hour into a mixture of 300 grams of commercial sodium sulphite, 375 c.c. of water, and 125 c.c. of methyl alcohol, boiling under reflux. The solid residue obtained by evaporation of the filtered solution is extracted with 80 per cent. alcohol and crystallised. The yield of sodium methanesulphonate containing a small proportion of sodium methyl sulphate is about 94 per cent., calculated according to the equation

$$Me_2SO_4 + Na_2SO_3 = MeSO_3Na + MeO{\cdot}SO_3Na.$$

The sulphonyl chloride is prepared by heating 100 grams of the sulphonate and 200 grams of phosphoryl chloride (phosphorus pentachloride may be used, but the reaction is rather vigorous) at 130—150° for 2 hours. The liquid is purified by fractional distillation and the portion, b. p. 152—159°, collected (yield about 60 grams).

The amide is prepared by saturating a cold benzene solution of the sulphonyl chloride with dry ammonia gas. The mixture is finally warmed, filtered, and the solvent distilled off. The residue is crystallised from benzene–alcohol, when the pure methanesulphonamide separates in colourless, monoclinic plates, m. p. 84—85° (Found: N = 15·0. Calc., N = 14·7 per cent.) (yield 30 per cent. of the weight of methyl sulphate used). It is soluble in most of the ordinary organic solvents, in water, and in aqueous alkalis.

Reaction with Benzenediazonium Chloride.—The experiment is conducted in the way previously described (*loc. cit.*), the materials being methanesulphonamide (19 grams) in water (400 c.c.) and sodium hydroxide (16 grams), and a solution of benzenediazonium chloride (18·6 grams of aniline, 60 c.c. of concentrated hydrochloric acid, and 100 c.c. of water; 14 grams of sodium nitrite and 60 c.c. of water). The yellow solid that first appears soon decomposes, and the phenylazoimide thereby produced (19 grams) is extracted with ether and purified in the usual way.

The aqueous portion is treated again with the same quantity of benzenediazonium chloride, the yellow precipitate collected, washed with water, dried (yield 15 grams), and recrystallised from dilute alcohol, separating in yellow needles, m. p. 71—72° (decomp.) (Found: N = 15·38; S = 17·21. $MeSO_2N:NPh$ requires N = 15·22; S = 17·39 per cent.).

In another experiment, the diazoamine was filtered off as soon as it formed, but it decomposed so rapidly that it could not be purified and analysed. Methanesulphinic acid could not be prepared by the methods previously described (*loc. cit.*).

Reaction with p-*Toluenediazonium Chloride.*—The quantities used are those of the preceding experiment, 21 grams of *p*-toluidine replacing 18·6 grams of aniline. The yellow, crystalline precipitate first formed soon partly decomposes into an oil, but not completely even on the addition of more alkali. It is filtered (16 grams) and recrystallised from dilute alcohol; m. p. 112—113° (decomp.) (Found: N = 14·32; S = 16·02. $MeSO_2{\cdot}N{:}N{\cdot}C_7H_7$ requires N = 14·14; S = 16·16 per cent.). The *p*-tolylazoimide passes into the filtrate and is extracted with ether and purified in the usual way (yield 6 grams).

Action of Benzenediazonium Chloride on Toluene-ω-sulphonamide.—The sulphonamide (8·5 grams), dissolved in 100 c.c. of water containing 4 grams of sodium hydroxide, is treated with benzenediazonium chloride solution (made from 4·7 grams of aniline). The yellow precipitate soon changes to dark brown and finally a tarry mass is formed, from which phenylazoimide (2 grams) is isolated by steam distillation.

In conclusion, the author thanks the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

THE UNIVERSITY, LEEDS. [*Received, April 10th*, 1924.]

CLXXXVIII.—*The Rotatory Dispersive Power of Organic Compounds. Part XI. The Molecular Weight of Ethyl Tartrate and the Origin of Anomalous Rotatory Dispersion in Tartaric Acid and its Derivatives.*

By THOMAS MARTIN LOWRY and JOHN OUTRAM CUTTER.

1. *Astbury's Theory of the Origin of Anomalous Rotatory Dispersion.* In a recent paper on "The Crystalline Structure and Properties of Tartaric Acid" (*Proc. Roy. Soc.*, 1923, **102**, 506) W. T. Astbury has put forward a theory of the origin of the anomalous rotatory dispersion of this acid which implies that, whilst the individual molecules of tartaric acid contain a dextrorotatory skeleton of carbon atoms, the crystals contain also a lævorotatory spiral formed by contiguous hydroxyl groups in adjacent molecules. He therefore suggests that the lævo-component of the rotation, which when superposed on the dextro-component gives rise to anomalous rotatory dispersion, may be produced by the presence, even in dilute solutions, of "strings of molecules, connected together at the hydrogen junctions" of the hydroxyl groups.

This theory is a revival in almost identical terms of the suggestion of Landolt in 1879 ("Optisches Drehungsvermögen," 1st ed., p. 58; compare Pribram, *Monatsh.*, 1888, **9**, 401; Hammerschmidt, *Z. Rübenzucker. Ind.*, 1890, **40**, 939; Wyrouboff, *Compt. rend.*, 1892, **115**, 832) that the mutarotation of the sugars is due to the slow decomposition of "crystal molecules" into "chemical molecules" of lower rotatory power, and appears to be equally opposed to the experimental evidence. If it were true, there should be an intimate relation between the degree of association of the acid and both its rotatory power and the character of its rotatory dispersion. There is already enough information in the literature to suggest that these relations do not, in fact, exist; but the new observations described below provide conclusive evidence that the development of the lævo-component of rotatory power cannot be due to any mere association or polymerisation of simple dextrorotatory molecules. In our opinion the explanation of this phenomenon is to be sought

in some intramolecular change of structure or configuration rather than in intermolecular action between contiguous molecules.

2. *Rotatory Power and Molecular Weight of Ethyl Tartrate.*

In the case of tartaric acid and its salts, the possibility of detecting polymerisation experimentally is complicated by the occurrence of the opposite process of ionic dissociation, which might easily mask the former change; but this difficulty does not arise in connexion with the esters. These also show anomalous dispersion, but with the additional advantages that (i) a much wider range of rotations can be observed than in the acid or its simple salts, and (ii) the anomalous dispersion can be expressed exactly by two terms of Drude's equation, whereas the acid itself shows small systematic deviations which suggest the presence of a third (? ionised) component, not present in the esters. The work of Bruhat (*Trans. Faraday Soc.*, 1914, **10**, 89) has, moreover, established the fact that *amorphous tartaric acid behaves in every way like a lower homologue of its methyl and ethyl esters.* For the purpose of this research, therefore, ethyl tartrate was selected as the most convenient material on which to test the crystallographic theory of anomalous dispersion; and formamide and benzene were chosen as solvents.

(a) *Formamide* gives higher dextrorotations than nearly all the other compounds which have been used as solvents for methyl or ethyl tartrate; their dispersions are, however, still highly complex. Thus, although ethyl tartrate gives quasi-hyperbolic curves in the visual region of the spectrum, the dispersion ratios are much too low to correspond with a simple dispersion; and the only solution which was examined photographically gave an obvious inflexion in the deep violet region (Lowry and Dickson, J., 1915, **107**, 1183). A solution of methyl tartrate in the same solvent showed a strongly-developed maximum in the blue (Lowry and Abram, J., 1915, **107**, 1193). Cryoscopic measurements of ethyl tartrate in formamide, however, show no slightest sign of polymerisation, the relation between concentration and freezing point being rigidly linear over the whole range from 0 to 16 per cent. Since the molecular weight of the solute remains accurately that of the simple molecule, it is clear that the lævorotatory component of the solution cannot be a mere polymeride of the ester.

(b) *Benzene* is interesting because the rotatory power of ethyl tartrate in this solvent is nearly the same as in the pure state (Patterson, J., 1902, **81**, 1099). The curve connecting concentration and rotatory power actually shows a shallow maximum at 10 per cent. and a shallow minimum at about 5 per cent. of ethyl tartrate. In dilute solutions, therefore, the rotatory power increases slightly

with the concentration. Cryoscopic measurements have shown, however, that this increase of dextrorotatory power is accompanied by a rapid polymerisation of the solute, which, according to Astbury's theory, should give rise instead to strong lævorotations.

(c) *Ethylene bromide* is a solvent in which the polymerisation of ethyl tartrate increases with the concentration even more rapidly than in the case of benzene (Winther, *Z. physikal. Chem.*, 1907, **60**, 584); but measurements of rotatory dispersion (Lowry and Dickson, *loc. cit.*) show that this polymerisation is accomplished by a diminution, instead of by an increase, of lævorotatory power.

(d) In *naphthalene* at 70°, the dextrorotatory power of ethyl tartrate is even higher than in formamide at 20° (Patterson, J., 1902, **81**, 1134); but the solute is polymerised (50 per cent. at a concentration of about 9 per cent.) in naphthalene at about 80° even more strongly than in benzene at about the same temperature.

The behaviour of ethyl tartrate in four typical solvents is thus directly opposed to the view that the lævorotatory component of tartaric acid and its esters is a mere polymeride of the dextrorotatory component. The facts appear to agree much more closely with the following propositions :

(i) The ester exists in isomeric dextro- and lævo-forms.*

(ii) The lævo-form tends to be produced in solvents which favour polymerisation.

(iii) This polymerisation, however, usually produces an increased dextrorotation or a decreased lævorotation.

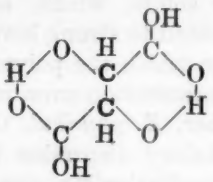
3. *Internal and External Co-ordination.*

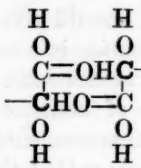
The preceding paragraphs have dealt with Astbury's theory in its most general form, namely, that anomalous rotatory dispersion in tartaric acid is due to an incomplete conversion of simple dextrorotatory molecules into a lævorotatory polymeride, the structure of which need not for the moment be considered. The particular form which he gives to that theory is, however, open to further criticism, since it is based upon assumptions that, from the chemical point of view, are improbable.

It has already been suggested by one of us (Lowry and Burgess, J., 1923, **123**, 2118) that the hydroxylic hydrogens of tartaric acid and its esters may be co-ordinated internally with the carbonyl groups, as in formula I, where these hydrogens are shown as bivalent (compare G. N. Lewis, "Valence," p. 109). In his crystallographic analysis, Astbury assumes that these carbonyl groups are in contact

* Longchambon (*Compt. rend.*, 1924, **178**, 951) has recently described the lævo- and dextro-rotatory forms of *d*-tartaric acid as α- and β-tartaric acid respectively.

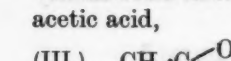
with the hydrogen atoms which are directly attached to the asymmetric carbon atoms, as in II.

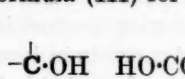
(I.) 

 (II.)

The hydroxylic hydrogens are shown as contiguous with the carboxylic hydrogens of another molecule, as may be seen by repeating the pattern shown in II, both above and below it.

We are not in a position to criticise the assumptions which have led to the adoption of this configuration for the crystalline acid *; but it is unlikely that either of these subsidiary linkages would have that maximum stability which would enable it to persist in solution. Any association in the liquid state must almost certainly depend, either on an external co-ordination between the carboxyl groups of two different molecules, as in Lewis's formula (III) for bimolecular acetic acid,

(III.) 

 (IV.)

or on an external co-ordination of carbonyl with hydroxyl, analogous to the internal co-ordination shown in I above. The hydrogens of two hydroxyl groups, arranged as in the scheme IV, would almost certainly repel, rather than attract, one another; and whilst this would not be incompatible with the possible nature of the contact at a plane of cleavage of the crystal, it is most unlikely that it would be selected as the most effective method for the polymerisation of individual molecules.

The fact that the anomalous rotatory dispersion of tartaric acid is not destroyed by esterification is wholly incompatible with Astbury's explanation of the origin of this phenomenon, but it could, of course, be reconciled with an external co-ordination of the hydroxyl of one molecule with a carbonyl group of an adjacent molecule. It is, therefore, not a valid argument against the general proposition that anomalous dispersion may be due to polymerisation, but only against the particular form in which the proposition was made.

* The method appears to depend on determining experimentally the linear dimensions of the "cells" containing the molecules of the acid, and then twisting the conventional molecular models until they can be fitted into these cells. The positions of the hydrogen atoms, in particular, are not deduced in any direct way from the *X*-ray data given in the paper.

EXPERIMENTAL.

4. *Materials.*—Determinations of the molecular weight of ethyl tartrate in ethylene bromide and in formamide have been made by Winther (*loc. cit.*), whilst determinations in benzene, *p*-xylene, and naphthalene have been made by Patterson (J., 1902, **81**, 1097, 1134). The observations now recorded were made with ethyl tartrate which had been purified by freezing until its freezing point was constant (Lowry and Cutter, J., 1922, **121**, 532), whilst the solvents were also crystallised to constant freezing point. The formamide, which melted at 2·2° and had a density 1·1321 at 15°, appears to have been much purer than that used by Winther, since its cryoscopic constant was 5·16° instead of 3·2°.

5. *Apparatus and Methods.*—The apparatus used was the standard Beckmann arrangement for the determination of depression of freezing point. The outer jacket was cooled by the aspiration of air through ethyl ether; complete control of the temperature was obtained by adjustment of the rate of aspiration. The inner tube containing the solvent and solute was guarded by calcium chloride tubes, and a slow stream of dry air was drawn over the surface of the liquid. This was found to be essential, even to obtain consistent freezing points of pure formamide. In the final determination in formamide it was necessary to inoculate the liquid in order to avoid excessive over-cooling; otherwise the procedure was as usual.

6. *Results.*

The published values of the cryoscopic constant of formamide vary from 3·20° (Winther) to 3·85° (Bruni and Trovanelli, *Gazzetta*, 1904, **34**, ii, 350). This constant was therefore redetermined, carbamide being used as the solute. Since compounds containing hydroxyl groups usually give normal molecular weights in hydroxylic solvents, it was expected that a compound containing an amino-group would give a normal molecular weight in formamide. In the following tables, p = percentage concentration, Δ = depression of freezing point, K = the cryoscopic constant, and M = the molecular weight.

Cryoscopic Constant for Carbamide in Formamide.

p	1·213	1·842	2·834	3·509	3·841	5·024	
Δ	1·035°	1·601°	2·446°	3·007°	3·295°	4·227°	
K	5·131	5·214	5·179	5·141	5·147	5·165	(mean 5·163)

Cryoscopic Constant for Ethyl Tartrate in Formamide.

p	1·320	2·628	3·653	11·641	16·070	
Δ	0·333°	0·657°	0·908°	2·924°	4·042°	
K	5·195	5·150	5·221	5·174	5·182	(mean 5·184)

Molecular Weight of Ethyl Tartrate in Benzene.

p	1·234	2·271	3·455	10·594	14·553	19·529
Δ	0·322°	0·527°	0·694°	1·965°	2·162°	2·845°
M.....	196	220	254	275	342	350

7. *Summary.*

(*a*) The cryoscopic constant of carefully-purified formamide, melting at 2·2°, is 5·16° per gram-mol. of carbamide in 1000 grams of solvent. Ethyl tartrate is unimolecular in this solvent up to a concentration of 16 per cent., the mean value of the cryoscopic constant being 5·18°. The dispersion curves are, however, strongly complex in character.

(*b*) The molecular weight of ethyl tartrate in benzene increases to nearly double its normal value at a concentration of about 20 per cent.; but the rotatory power increases up to about 10 per cent. and then decreases again.

(*c*) In ethylene bromide, the polymerisation of ethyl tartrate is more rapid than in benzene, but is accompanied by a progressive diminution of lævorotatory power.

(*d*) Ethyl tartrate gives even higher dextrorotations in naphthalene at 70° than in formamide at 20°; but it is more strongly polymerised in this solvent at 80° than in benzene at the same temperature (Patterson).

(*e*) These results are incompatible with Astbury's suggestion that the dextrorotatory component of tartaric acid is a single molecule, whilst the lævorotatory component is a polymeride in which the structure of the crystal is in part maintained.

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CLXXXIX.—*Sedimentation of Bentonite.*

By HUBERT FRANK COWARD.

BENTONITE is a natural silicate of aluminium of somewhat variable composition (compare *Bull. Imp. Inst.*, 1922, **20**, 344). On immersion in water, it swells considerably, and in the course of a few minutes a small piece will absorb some six to eight times its own volume of water and assume a jelly-like appearance. When this mass is shaken with water, a milky suspension is formed, and this rapidly deposits a small amount of crystalline matter, adventitious concomitants of the colloidal mineral.

A sample of bentonite, part of a consignment from Newcastle, Wyoming, U.S.A., presumably from the well-known deposits of

the Laramie Basin, Wyoming, was supplied to the author by the Department of Scientific and Industrial Research. The milky aqueous suspension was examined under the microscope and was found to contain particles of various sizes, the smallest being in Brownian motion. On standing, the coarse matter settled, but the finer particles remained in suspension and the liquid was turbid for many months.

On the addition of acids, alkalis, or salts to a suspension of bentonite, no difference was apparent in its behaviour, as described above, until a critical strength of solute was reached; beyond this critical point, the suspended matter settled somewhat rapidly, leaving a clear supernatant liquid above a gelatinous precipitate of considerably greater bulk than that deposited from water. This flocculating power appears to be confined to electrolytes, for $N/4$-mercuric chloride and $N/4$-phenol and even $6{\cdot}3M$-formaldehyde failed to clear the suspension, whilst much more dilute solutions of the stronger electrolytes were sufficient to cause clearing.

The clearing power of several electrolytes was therefore examined in some detail. For the experiments, a suspension of the finer particles of the mineral was made by soaking a sample in water, well shaking, allowing to settle for several hours, and decanting the supernatant liquid. This was found to contain 6·88 grams of dry bentonite per litre, which is equivalent to somewhat more of the natural substance, the water content of which was 18·5 per cent. Equal volumes of this suspension and of chosen strengths of electrolyte solution were mixed. The electrolyte solutions were made in the series $2N$, N, $N/2$, $N/4$, $N/8$, $N/16$, $N/32$, $N/64$, $N/128$, $N/256$, etc., which correspond in the case of a completely dissociated acid with the arithmetical series of values for p_{H} — 0·30, 0, + 0·30, 0·60, 0·90, 1·20, 1·51, 1·81, 2·11, 2·31, etc.

Sedimentation of a bulky gelatinous nature, leaving the supernatant liquor clear, was observed at the end of 1 day from solutions of strengths (after admixture) stated in the table, but not with solutions of half these strengths or weaker.

To provide an interpretation of the figures in the second column, a series of measurements was made of the relative motion, under constant electric stress, of bentonite suspensions in aqueous solutions of sodium hydroxide, sulphuric acid, sodium chloride, and phenol. In each case the movement was towards the positive pole and therefore the suspended particles were negatively charged in these solutions. The rate of movement was, however, decreased gradually by increase in the concentration of either acid, alkali, or salt (but not by the non-electrolyte phenol), until flocculation made further observation impossible.

Solute.	Precipitating concentration (equivalent normality).	Probable active ion.	Concentration of probable active ion (gram-atom per litre).
Hydrochloric acid	$N/128$	$H^{\cdot}$	1/128
Sulphuric acid	$N/128$	$H^{\cdot}$	1/128
Acetic acid	N		
Ammonia	N		
Sodium hydroxide	$N/32$	$Na^{\cdot}$?	1/32
Barium hydroxide	$N/256$	$Ba^{\cdot\cdot}$	1/512
Sodium chloride	$N/64$	$Na^{\cdot}$	1/64
Barium chloride	$N/256$	$Ba^{\cdot\cdot}$	1/512
Aluminium chloride	$N/256$	$Al^{\cdot\cdot\cdot}$	1/768
Quinine hydrochloride	$N/2048$		
Methylene-blue hydrochloride	$N/4096$		
Mercuric chloride	No gelatinous flocculation up to $N/4$		
Phenol	" " " "		$N/4$
Formaldehyde	" " " "		$6{\cdot}3M$

It appears, therefore, that in every case we must look for an explanation of the flocculation in the adsorption of positive ions by the particles. As would be deduced from this, we observe equal precipitating concentrations ($N/128$) for hydrochloric and sulphuric acids; the solutions of the two strong alkalis are very different in flocculating power, since this does not depend on the hydroxyl-ion concentration, but rather on the metal-ion concentration, and, as is usual in such cases, the barium-ion is effective at much lower concentrations than the sodium-ion. Similarly in the case of the salts, it is not the chlorine-ion concentration which governs the flocculation, for, if so, sodium and barium chlorides would precipitate at the same normality. The negative ion is, however, not completely without influence, for sodium hydroxide is a less effective flocculating agent than sodium chloride. The difference becomes less, perhaps nil, when the positive ion is the strong precipitant barium; for barium hydroxide and barium chloride cause flocculation at the same concentration.

When the positive ion is large, as in the case of the hydrochlorides of quinine and methylene-blue, remarkably small concentrations are sufficient for flocculation, and the simple regularities noted above are overshadowed.

Variation of Amount of Bentonite in Suspension.—Experiments were conducted with suspensions containing the following amounts of dry bentonite: 3·44, 1·72, 0·86, 0·43, and 0·21 grams per litre. Sedimentation was more rapid, the thinner the suspension; but in each case $N/32$-sodium hydroxide caused complete flocculation, whilst $N/64$-sodium hydroxide was insufficient in any case. With hydrochloric acid, sedimentation was likewise more rapid the thinner the suspension, and the critical concentration of acid was independent of the amount of bentonite in suspension.

The Time Factor in Flocculation.—The rate of sedimentation, in the presence of sufficient electrolyte to produce clearing of the liquid, varied, not only with the amount of suspensoid, but also with the nature of the flocculating agent, and even with the width of the vessel used for experiment. Barium and aluminium chlorides and barium hydroxide were most effective in this respect, whilst ammonia and acetic acid were least effective. For example, in the case of a suspension of 3·44 grams of bentonite per litre, the former three substances in suitable concentration produced clearing of about one-third of the liquid in the course of an hour, whilst several days had to elapse before much clearing was observed with ammonia and acetic acid in certain concentrations which ultimately produced complete deposition.

The tabulated figures for limit concentration for clearing the suspensions refer to observations made at the end of 1 day after preparation of the mixture. It was found that in the course of 1 month several of the suspensions which showed no clearing in 1 day had then become clear: hydrochloric and sulphuric acids in $N/256$ concentration (but not more dilute) produced clearing; baryta, sodium chloride, and barium chloride showed no change in the limit figure; aluminium chloride at $N/512$ showed clarification, and this fact establishes the superior precipitating power of the aluminium-ion over that of the barium-ion, which was not proved by the 1-day experiments. Ammonia and acetic acid, with their slow action, gave clearing in solutions as weak as $N/16$ after 1 month, in contrast with the 1-day results which required N-solutions for clarification.

An experiment with quinine hydrochloride showed the very bulky nature of the precipitate in this case. In test-tubes containing 3·44 grams of bentonite per litre in presence of $N/32$- to $N/256$-quinine hydrochloride, the clearing was not more than 18 per cent. of the total liquid height during 8 days; but there was 36 per cent. clearing in only 2 days in an ordinary 500 c.c. glass measuring cylinder. The swollen particles seemed to form a loosely cohesive bridge across the tube, and this would naturally settle more rapidly in the wider tube.

Reversibility of the Precipitation.—The gelatinisation and complete deposition of bentonite suspensions appear to be reversible, as shown by the following experiments: (i) A deposited suspension in the presence of $N/32$-sodium hydroxide was diluted eight-fold with distilled water and shaken. The resultant suspension remained cloudy, depositing in the course of some weeks only a part of its bentonite, and this was in the more compact form observed with solutions insufficiently strong to cause gelatinisation and

precipitation. (ii) Equal volumes of the mixtures containing $N/64$-sodium hydroxide and $N/64$-hydrochloric acid were mixed together to form a $N/128$-sodium chloride mixture. The new suspension behaved like a freshly made salt mixture of the same strength, *i.e.*, the liquid remained cloudy for some weeks.

The $N/128$-hydrochloric acid mixture diluted to $N/512$ was different. In spite of the dilution to a strength at which gelatinous sedimentation would not be expected, this nevertheless occurred. The experiments quoted below on sorption by bentonite may afford an explanation of this anomaly.

Sorption by Bentonite.—A suspension in sodium hydroxide which had settled showed no change in concentration of the supernatant liquid, in an experiment which would have detected the removal of 1 mg. of sodium hydroxide per gram of bentonite. On the other hand, $N/64$-hydrochloric acid became weaker to an extent corresponding with the sorption of 24 mg. of hydrogen chloride per gram of bentonite. This may be due to chemical reaction with some constituent of the mineral, or to adsorption, but in any case does not cause such alteration in the concentration of the solution as to make any difference in the figures given in the table.

Summary and Conclusions.

A sample of bentonite from Wyoming was found to form aqueous suspensions, the smaller particles of which were in Brownian motion. This suspensoid was negatively charged, and the charge decreased in the presence of increasing quantities of electrolytes, whether they were acid, alkali, or salt, until at sufficient concentration the bentonite was wholly sedimented in a highly gelatinised form. The flocculation was reversible.

Bentonite is therefore a typical negative suspensoid colloid, and as the preparation of its suspension is merely a matter of shaking with water after a few minutes' soaking, it may prove useful as material for investigations in the chemistry of colloids.

THE TOOTAL BROADHURST LEE CO., LTD.,
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CXC.—*Studies in Optical Superposition. Part V.** d-sec.-*Octyl* i-*Tartrate.*

By T. S. Patterson and Charles Buchanan.

In the course of their work on the resolution of *sec.*-octyl alcohol, Pickard and Kenyon (J., 1911, **99**, 68) prepared, from the active alcohol, the esters of *d*- and *l*-tartaric acid in order to compare their rotations with that of the corresponding ester of the *meso*-acid. They were unsuccessful, however, in making this last compound, finding that it decomposed on distillation.

In connexion with some work which we have recently been carrying out, we had occasion to prepare *d-sec.*-octyl alcohol, and we thought it worth while to make another attempt to obtain *d-sec.*-octyl *i*-tartrate, since the rotations of the three *sec.*-octyl tartrates should be of considerable interest. The *d-sec.*-octyl alcohol was obtained by Kenyon's method (J., 1922, **121**, 2540). It boiled at 87°/17 mm., and had the rotation $\alpha^{16°}_{\text{Hg. gr.}}$ (200 mm.) = + 19·45°.

d-sec.-*Octyl* i-*Tartrate.*—The ester was prepared by passing dry hydrogen chloride for 20 hours through a mixture of 10 grams of *i*-tartaric acid with 30 grams of *d-sec.*-octyl alcohol at 80—90°. The mixture was then distilled under reduced pressure until the thermometer reached 100°, to remove excess alcohol. The residue was dissolved in benzene, and after the solution had been washed with dilute sodium carbonate solution † and with water, and dried with calcium chloride, the bulk of the solvent was distilled off and the total residue distilled under about 4 mm. pressure until the thermometer registered 140°, to remove all excess benzene and alcohol. The residue was distilled in very small quantities (about 2 c.c.) at a time under 4 mm. pressure; there was some frothing at the commencement of the distillation in each case, but otherwise the liquid distilled easily, and, on standing, the distillate solidified. The total distillate was redistilled, three fractions being taken: (1) b. p. 200—208°/about 4 mm., m. p. about 30°, (2) b. p. 208°/about 4 mm., m. p. 33°, (3) main fraction, b. p. 208°/about 4 mm., m. p. 33°. The total yield was about 8 grams. On hydrolysis,

* Part IV, J., 1915, **107**, 142.

† This precipitated a solid, presumably sodium *d-sec.*-octyl *i*-tartrate, which was very sparingly soluble in cold water but readily soluble on heating and which crystallised in glistening plates. 0·1012 Gram made up to 20 c.c. with water at 20° gave a rotation of −0·024° in a 2 dcm. tube, whence $\alpha^{20°}_{\text{Hg. gr.}}$ = − 2·37°. On hydrolysis with 0·0994*N*-sodium hydroxide solution, 0·2013 gram required 7·27 c.c. Theoretical for $NaO_2C{\cdot}[CH{\cdot}OH]_2{\cdot}CO{\cdot}O{\cdot}C_8H_{17}$ is 7·13 c.c.

0·2601 gram of *d-sec.*-octyl *i*-tartrate required 13·88 c.c. of 0·1007 *N*-sodium hydroxide in methyl alcoholic solution (calc., 13·80 c.c.).

Rotation of d-sec.-*Octyl* i-*Tartrate.*

t	17°	35·5° *	36·5°	48° *	64° *	85·5° *
Densities.....	0·9998	0·9849	0·9840	0·9743	0·9618	0·9442

* Experimental.

	$t = 17°$. $l = 30·48$ mm.			$t = 36·5°$. $l = 30·49$ mm.		
λ.	Obs. rot.	[α].	[*M*].	Obs. rot.	[α].	[*M*].
6716·3	+ 0·148°	+ 0·486°	+ 1·82°	+ 0·147°	+0·490°	1·83°
6234·3	+ 0·14	0·459	1·72	0·237	0·790	2·98
5790·3	+ 0·124	0·407	1·52	0·212	0·706	2·64
5460·7	+ 0·056	0·184	0·69	0·19	0·633	2·37
4959·7	− 0·012	− 0·039	− 0·15	0·089	0·297	1·11
4358·3	− 0·448	− 1·470	− 5·50	− 0·09	0·303	− 1·13

From these data the value for the specific rotation of the homogeneous ester for sodium light at 17° is + 0·42° and on comparing this with the values found by Pickard and Kenyon we have the following results :

	d-Tartrate.	*l*-Tartrate.	Mean.	*i*-Tartrate.
$[\alpha]_D^{17°}$ *d-sec.*-octyl	+ 24·06°	+ 2·06°	+ 13·06°	+ 0·42°

If the so-called principle of optical superposition were true, the rotation of the *i*-compound should equal the mean of the rotations of the *d*- and *l*-compounds.

Since the low rotation value of the *i*-tartrate might be due to racemisation of the alcohol, 5 grams of the ester were hydrolysed by boiling for 2 hours with sodium carbonate solution. Some 2 c.c. of alcohol having $\alpha_{\text{Hg. gr.}}^{18·5°}$ (30·48 mm.) = + 2·64° were recovered, the value for the pure alcohol in similar circumstances being + 2·95°. It is clear that, if this is not due merely to imperfect purification of the small quantity of material, any racemisation which has occurred would not be sufficient to account for the difference between the mean value of Pickard and Kenyon's results for the octyl esters of *d*- and *l*-tartaric acid, and ours for that of the octyl ester of *i*-tartaric acid. These results therefore form rather a striking proof of the non-validity of the principle of optical superposition.

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UNIVERSITY OF GLASGOW. [*Received, April 2nd,* 1924.]

CXCI.—*The Formation of Triphenylmethylphosphinic Acid from Triphenylmethoxyphosphorus Dichloride.*

By David Runciman Boyd and Frederick James Smith.

The action of an alcoholic solution of potassium hydroxide upon triphenylmethoxyphosphorus dichloride, $(C_6H_5)_3C\cdot O\cdot PCl_2$, gives rise to an acid (Boyd and Chignell, J., 1923, **123**, 813), which, from its mode of formation, was assumed to be triphenylmethylphosphorous acid, $(C_6H_5)_3C\cdot O\cdot P(OH)_2$. Further investigation of this compound has shown, however, that its properties are not in harmony with this constitution.

When a solution of the acid in one equivalent of sodium hydroxide is titrated with a solution of sodium hydroxide, the curve showing change of p_H with increase of alkali concentration indicates the existence of a second salt. The acid is therefore dibasic, and in agreement with this view a dipotassium salt and a corresponding barium salt have been prepared. Since alkylphosphorous acids of the type $R\cdot O\cdot P(OH)_2$ are monobasic, it follows that the substance obtained from triphenylmethoxyphosphorus dichloride cannot belong to this group of compounds. An alternative formula is that of triphenylmethylphosphinic acid, $(C_6H_5)_3C\cdot PO(OH)_2$. This constitution is in agreement both with the observed basicity of the acid and with its general chemical character, the acid being stable, not only towards aqueous alkalis, but also towards acid hydrolysing agents. Concentrated hydrochloric acid at 170°, and boiling aqueous hydriodic acid are without action upon it. On heating with soda-lime, triphenylmethane is formed, a reaction characteristic of phosphinic acids. The hydrolysis of the phosphorus chloride under the influence of alcoholic potash must therefore be accompanied by a molecular rearrangement, somewhat similar in character to that which diethyl sulphite undergoes when acted upon by aqueous potassium hydroxide (Rosenheim and Liebknecht, *Ber.*, 1898, **31**, 405; Rosenheim and Sarow, *Ber.*, 1905, **38**, 1298).

$$(C_6H_5)_3C\cdot O\cdot P^{III}Cl_2 \xrightarrow[\text{in alcohol}]{KOH} (C_6H_5)_3C\cdot P^{V}O(O\cdot C_2H_5)(OK)$$

$$S^{IV}O(O\cdot C_2H_5)_2 \xrightarrow[\text{in water}]{KOH} C_2H_5\cdot S^{VI}O_2\cdot OK$$

A further investigation of the reaction between phosphorus trichloride and triphenylcarbinol has shown that triphenylmethylphosphinic acid is produced in small quantity when the mixture of products formed by the action of phosphorus trichloride upon triphenylcarbinol is treated with water. The formation of a phosphinic acid in this way is a very unusual occurrence, and is not

easily reconciled with the customary equation (Menschutkin, *Annalen*, 1866, **139**, 343) for the reaction between an alcohol and excess of phosphorus trichloride:

$$R{\cdot}OH + PCl_3 = R{\cdot}O{\cdot}PCl_2 + HCl.$$

Michaelis, who showed (*Ber.*, 1901, **34**, 1298) that oxymethylenecamphor yields a phosphinic acid by treatment with phosphorus trichloride, accounted for the abnormal course of the reaction by the assumption that the oxymethylenecamphor functions in this case as an aldehyde (compare Conant, *J. Amer. Chem. Soc.*, 1920, **42**, 2337). No such explanation is possible in the case of triphenylcarbinol, since this alcohol cannot isomerise into an aldehyde or ketone.

In view, however, of the unsaturated condition of the phosphorus atom in phosphorus trichloride, it appears not improbable that the first step in the reaction between an alcohol and the trichloride of phosphorus is the formation of an additive compound; and that this, by elimination of hydrogen chloride, gives rise to the final products. If this hypothesis be adopted, two possibilities arise:

$$(1)\ R{\cdot}OH + PCl_3 = Cl_3P{<}\begin{matrix}OR\\H\end{matrix} = Cl_2P{\cdot}OR + HCl.$$

$$(2)\ R{\cdot}OH + PCl_3 = Cl_3P{<}\begin{matrix}OH\\R\end{matrix} = Cl_2RP{:}O + HCl.$$

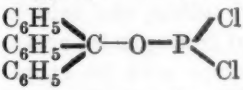
Equation (1) represents the normal reaction between phosphorus trichloride and an alcohol. But if the alcohol possesses a pronounced basic character, and has therefore a certain tendency to dissociate into R· and ·OH, it may be anticipated that reaction (2) also will take place. In the case of triphenylcarbinol the reaction proceeds according to equation (1) to the extent of 78 per cent. of the carbinol employed, whilst about 5 per cent. of the carbinol appears to react according to equation (2).

In considering the mechanism of the abnormal hydrolysis

$$Ph_3C{\cdot}O{\cdot}PCl_2 \longrightarrow Ph_3C{\cdot}PO(OEt){\cdot}OK$$

it is important to notice that the phenomenon is intimately related to the unusual stability of the phosphorus chloride towards aqueous alkalis. No migration of the radical R occurs during the hydrolysis of compounds of the type $R{\cdot}O{\cdot}PCl_2$ when, as usually happens, these compounds are easily attacked by water. It would appear, therefore, that an important factor in determining whether the hydrolysis of a given phosphorus chloride will proceed normally or will be accompanied by a movement of the radical R, is the degree of stability which the compound in question exhibits toward water and aqueous alkalis.

The stability towards hydrolysing agents shown by triphenylmethoxyphosphorus dichloride may be due in part to steric hindrance arising from the proximity of the three phenyl groups to the phosphorus atom. If, however, the first step in the hydrolysis of a compound of the type $R{\cdot}O{\cdot}PCl_2$ is, as has been suggested, the formation of an additive compound, then the stability of triphenylmethoxyphosphorus dichloride may also be attributed to a diminution in the free affinity of the phosphorus atom resulting from the enhanced valency demand of the oxygen, as indicated by the formula



When reaction does occur, under the influence of hot alcoholic potash, the disturbance of the molecule due to the addition of the elements of alcohol and the subsequent splitting off of hydrogen chloride, might not unnaturally lead to a movement of the triphenylmethyl group from oxygen to phosphorus: thus giving rise to a more stable compound in which the phosphorus atom is quinquevalent.

$$Ph_3C{\cdot}O{\cdot}P^{III}Cl_2 + Et{\cdot}OH = Ph_3C{\cdot}O{\cdot}P^{V}Cl_2H{\cdot}OEt.$$
$$Ph_3C{\cdot}O{\cdot}PCl_2H{\cdot}OEt + KOH = Ph_3C{\cdot}POCl{\cdot}OEt + KCl + H_2O.$$
$$Ph_3C{\cdot}POCl{\cdot}OEt + 2KOH = Ph_3C{\cdot}PO(OEt){\cdot}OK + KCl + H_2O.$$

EXPERIMENTAL.

Triphenylmethoxyphosphorus Dichloride.—An improved yield is obtained if the crude product (*loc. cit.*) is digested for some hours on a water-bath with aqueous ammonia. Any triphenylchloromethane, which may be present, is thus converted into triphenylcarbinol. The solid is then collected, washed with water, drained, and digested for some hours with a considerable volume of ether, in which triphenylcarbinol is easily soluble. The undissolved phosphorus chloride is filtered off, and after washing with ether is obtained in an almost pure condition. The ammoniacal filtrate on acidification gives a precipitate of triphenylmethylphosphinic acid. In one experiment 20·75 grams of triphenylmethoxyphosphorus dichloride and 1·2 grams of triphenylmethylphosphinic acid were obtained from 20 grams of triphenylcarbinol.

Triphenylmethylphosphinic Acid.—The acid prepared by the action of alcoholic potassium hydroxide upon triphenylmethoxyphosphorus dichloride according to the method previously described contains varying proportions of the monoethyl ester, $Ph_3C{\cdot}PO(OEt){\cdot}OH$ (Found: in a specimen, m. p. 227—232°, OEt = 6·17 per cent., indicating the presence of about 50 per cent. of ethyl ester).

The pure acid is most conveniently prepared as follows. The precipitate obtained on acidifying the solution of the crude acid in caustic potash is dried in a steam-oven, and then boiled for an hour with a mixture of acetic acid and concentrated hydriodic acid (3 grams of acid, 15 c.c. of acetic acid, and 8 c.c. of hydriodic acid). The solution, on cooling, deposits large, prismatic crystals of triphenylmethylphosphinic acid. The crystals are washed with water containing sulphurous acid in order to remove iodine, and then with dilute hydrochloric acid. After a further washing with a little alcohol and finally with ether, the acid is obtained almost pure. It may be recrystallised from glacial acetic acid, or from benzene. When free from admixture with its ethyl ester, it melts at 275° (Found : C = 70·16; H = 5·65; P = 9·62. $C_{19}H_{17}O_3P$ requires C = 70·33; H = 5·30; P = 9·57 per cent.).

The yield of phosphinic acid is considerably improved by using 5 to 6 (in place of 3) molecular proportions of potassium hydroxide for 1 mol. of phosphorus chloride. In one experiment, using 3·5 grams of potassium hydroxide, dissolved in 35 c.c. of 98 per cent. alcohol, and 4 grams of phosphorus chloride, the yield of crude acid was 3·1 grams (80 per cent.).

Dipotassium triphenylmethylphosphinate, $Ph_3C{\cdot}PO(OK)_2,3H_2O$, separated in lustrous leaflets on cooling a solution of the acid in hot aqueous potassium hydroxide; it was washed with absolute alcohol until the washings were neutral, and dried in a vacuum (Found : P = 6·82, 7·14; K = 16·92; H_2O = 11·55. $C_{19}H_{15}O_3PK_2,3H_2O$ requires P = 6·83; K = 17·18; H_2O = 11·90 per cent.).

Barium triphenylmethylphosphinate, $Ph_3C{\cdot}PO_3Ba,4H_2O$, a white precipitate obtained on adding barium chloride to an aqueous solution of the potassium salt, was dried in a vacuum (Found : Ba = 25·66; H_2O = 14·02. $C_{19}H_{15}O_3PBa,4H_2O$ requires Ba = 25·80; H_2O = 13·59 per cent.).

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, April 23rd*, 1924.]

CXCII.—*Halogenation of* s.-*Dipotassium Tetranitroethane.*

By LOUIS HUNTER.

BROMINATION of *s.*-dipotassium tetranitroethane, with formation of a tribromotrinitroethane, has been described by Scholl and Brenneisen (*Ber.*, 1898, **31**, 642). Further products of halogenation of this salt are now described.

Chlorine reacts with aqueous *s*.-dipotassium tetranitroethane to form the hitherto unknown s.-*dichlorotetranitroethane*, in accordance with the equation

$$\begin{matrix}\mathrm{CK(NO_2)_2}\\ \mathrm{CK(NO_2)_2}\end{matrix} + 2\mathrm{Cl_2} = \begin{matrix}\mathrm{CCl(NO_2)_2}\\ \mathrm{CCl(NO_2)_2}\end{matrix}\ (\mathrm{I.}) + 2\mathrm{KCl}.$$

The chloronitro-compound shows the usual reactions of " positive " halogen characteristic of the *gem*-halogenonitroparaffins; thus it decomposes with caustic potash or potassium iodide with regeneration of *s*.-dipotassium tetranitroethane,

$$(\mathrm{I.}) + 4\mathrm{KOH(or\ 4KI)} = \begin{matrix}\mathrm{CK(NO_2)_2}\\ \mathrm{CK(NO_2)_2}\end{matrix} + 2\mathrm{KClO} + 2\mathrm{H_2O(or} + 2\mathrm{KCl} + 2\mathrm{I_2}),$$

and reacts vigorously with potassium cyanide, being more or less completely hydrolysed to carbonate and cyanogen chloride.

ααβ-Tribromo-αββ-trinitroethane, which was obtained by the above authors by the action of bromine on ice-cold aqueous *s*.-dipotassium tetranitroethane, can be reconverted into the latter by the action of potassium iodide, the potassium nitrite formed by a side decomposition of the tribromotrinitroethane being the nitrating agent :

$$\begin{matrix}\mathrm{CBr_2(NO_2)}\\ \mathrm{CBr(NO_2)_2}\end{matrix} + 4\mathrm{KI} + \mathrm{KNO_2} = \begin{matrix}\mathrm{CK(NO_2)_2}\\ \mathrm{CK(NO_2)_2}\end{matrix} + 3\mathrm{KBr} + 2\mathrm{I_2}.$$

This example of internal nitration is not unique, and can be compared with the decomposition of bromopicrin by potassium cyanide, iodide, or hydroxide (Scholl and Brenneisen, *loc. cit.*; Hunter, J., 1923, **123**, 543), and the action of caustic potash on mono- or di-bromonitropropane (ter Meer, *Annalen*, 1876, **181**, 1).

In an attempt to prepare the bromine analogue of *s*.-dichlorotetranitroethane, aqueous *s*.-dipotassium tetranitroethane was treated with bromine vapour in a manner similar to that adopted in the case of chlorine. Instead of a derivative of ethane, however, a yellow oil, identical in all its properties with dibromodinitromethane, was formed in accordance with the equation

$$\begin{matrix}\mathrm{CK(NO_2)_2}\\ \mathrm{CK(NO_2)_2}\end{matrix} + 3\mathrm{Br_2} = 2\mathrm{CBr_2(NO_2)_2} + 2\mathrm{KBr}.$$

The same oil is produced by using bromine water instead of the vapour, and there is little doubt that the oil obtained by Allsop and Kenner (J., 1923, **123**, 2313) under similar conditions was dibromodinitromethane.

The stability of *s*.-dipotassium tetranitroethane towards iodine is well illustrated in the preparation of this salt from bromopicrin by the action of potassium iodide (Hunter, *loc. cit.*), the iodine

liberated during the reaction being without effect on the organic salt. The equation proposed (*loc. cit.*) to express this reaction requires a preliminary formation of potassium nitrite by a side decomposition. In an attempt to increase the yield of *s.*-dipotassium tetranitroethane from bromopicrin by the previous addition of potassium nitrite to the mixture, it was found that the amount of the ethane salt was diminished rather than increased, due to a simultaneous formation of potassium iododinitromethane. The formation of the latter salt may be due to decomposition of *s.*-dipotassium tetranitroethane under the conditions of the experiment, in the sense of the equation

$$\begin{matrix}\mathrm{CK(NO_2)_2}\\ \mathrm{CK(NO_2)_2}\end{matrix} + 2\mathrm{I} = 2\mathrm{CKI(NO_2)_2},$$

but it is more probably due to the attack of the liberated iodine on some intermediate substance formed by the interaction of bromopicrin and potassium iodide. Salts other than potassium nitrite (*e.g.*, potassium cyanide, acetate, sulphite) failed to bring about a similar change.

Experimental.

s.-Dichlorotetranitroethane.—Since *s.*-dipotassium tetranitroethane is decomposed by acids (Scholl and Brenneisen, *loc. cit.*), chlorination of the salt was carried out in presence of sodium acetate to reduce mineral acidity. Without this precaution very poor yields were obtained.

A slow stream of chlorine was bubbled through a solution of *s.*-dipotassium tetranitroethane (3 grams) and sodium acetate (3 grams) in water (300 c.c.), cooled in a freezing mixture. A white, curdy solid immediately began to separate, and after a short time the yellow solution became colourless. The solid was rapidly washed with ice-cold water, dried on a porous plate, and exposed to the air for a short time to remove a trace of dichlorodinitromethane (yield 2·5 grams).

s.-Dichlorotetranitroethane thus prepared is a snow-white, amorphous powder, very soluble—frequently with decomposition—in organic solvents. It readily sublimes at the ordinary temperature to form star-shaped crystals, and is best purified by sublimation. It begins to decompose at 60—65° with evolution of oxides of nitrogen, and melts sharply at 107° (Found : Cl = 25·63; N = 19·70. $C_2O_8N_4Cl_2$ requires Cl = 25·45; N = 20·07 per cent.). It is volatile in steam with partial decomposition, and is slowly converted by boiling water into carbon dioxide, oxides of nitrogen, hydrochloric acid, and dichlorodinitromethane, which, on treat-

ment in alcoholic solution with powdered potassium iodide, yields potassium chlorodinitromethane, explosion point 85° (see Gotts and Hunter, this vol., p. 442). A similar decomposition occurs on heating in the dry state.

Action of Potassium Hydroxide.—*s*.-Dichlorotetranitroethane (1 gram), shaken with 50 per cent. aqueous potassium hydroxide (10 c.c.), was slowly converted into a yellow, soluble salt, a strong odour similar to that of chloropicrin being developed. After standing, the mixture was diluted with water (20 c.c.) and the precipitate crystallised from the liquor. It was obtained as a yellow, crystalline powder, explosion point 268°, exhibiting all the properties of *s*.-dipotassium tetranitroethane. Weight 0·5 gram (Found : K = 27·3. Calc., K = 27·3 per cent.). The alkaline filtrate contained chloride and chlorate.

Action of Potassium Iodide.—Finely powdered *s*.-dichlorotetranitroethane (1 gram) was slowly added with stirring to 50 per cent. aqueous potassium iodide (10 c.c.). Iodine was immediately liberated and a yellow, amorphous salt precipitated. Towards the end of the addition the reaction became vigorous and carbon dioxide was evolved. After standing, the precipitate was filtered and washed free from iodine, when it formed an orange-yellow powder free from halide. Explosion point, 274°; weight, 0·45 gram (Found : K = 26·6. Calc., K = 27·3 per cent.).

On similar treatment with potassium cyanide, *s*.-dichlorotetranitroethane reacted vigorously with evolution of cyanogen chloride. A black powder separated which proved to be inorganic, the filtrate containing carbonate, nitrite, and chloride.

Bromination of s.-*Dipotassium Tetranitroethane.*—A current of air was aspirated over liquid bromine and bubbled through an aqueous solution of equal parts of sodium acetate and *s*.-dipotassium tetranitroethane, cooled in a freezing mixture, until the solution was decolorised. The yellow oil was separated, washed, and dried. Its weight was only about half that expected from the equation (*q. v.*). Although a bromine analysis was not sufficient to distinguish between dibromodinitromethane and tribromotrinitroethane [Found : Br = 60·6. $CBr_2(NO_2)_2$ requires Br = 60·6. $C_2Br_3(NO_2)_3$ requires Br = 59·7 per cent.], the oil was shown to be the former by decomposition in alcoholic solution with potassium iodide, when potassium bromodinitromethane was obtained, explosion point 145° (Found : K = 17·56. Calc., K = 17·49 per cent.). The tribromotrinitroethane was shown to behave differently.

Action of Potassium Iodide on ααβ-Tribromo-αββ-trinitroethane.—This compound was prepared by bromination of *s*.-dipotassium tetranitroethane by Scholl and Brenneisen's method (*loc. cit.*). They

have already investigated its action towards potassium hydroxide and potassium carbonate.

The tribromotrinitroethane (1 gram) was slowly added with stirring to ice-cooled 25 per cent. aqueous potassium iodide (20 c.c.), when iodine was liberated and a slight evolution of carbon dioxide noticed; after standing, the precipitated salt was collected and washed free from iodine. It was almost pure *s.*-dipotassium tetranitroethane (0·3 gram), explosion point 267° (Found : K = 26·8. Calc., K = 27·3 per cent.).

The bromonitro-compound reacted vigorously with aqueous potassium cyanide with formation of cyanogen bromide, carbon dioxide, and a black, inorganic residue.

Preparation of Potassium Iododinitromethane from Bromopicrin.—Although best prepared from potassium dinitromethane (Gotts and Hunter, *loc. cit.*), this compound can be obtained from bromopicrin as follows. A solution of potassium iodide (15 grams) and potassium nitrite (6 grams) in water (60 c.c.) was mixed with alcohol (250 c.c.), and bromopicrin (10 grams) slowly added, iodine being immediately liberated. The first crystalline precipitate, consisting of pure *s.*-dipotassium tetranitroethane (explosion point 268°), was filtered off; after some hours, a second crop of crystals, consisting of the above potassium salt and potassium iododinitromethane, was deposited. On crystallising from hot water, potassium iododinitromethane was obtained as orange leaflets, exploding at 154—156° (Found : K = 14·50; I = 46·92. Calc., K = 14·44; I = 47·03 per cent.). Weight of ethane salt, 1·2 grams; and of potassium iododinitromethane, 1·0 gram. It yielded a sparingly soluble silver salt, exploding at 104—106° (Found : Ag = 32·3. Calc., Ag = 31·86 per cent.).

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CXCIII.—*Studies in Mutual Solubility. Part III. The Mutual Solubility of Glycerol and Amino- and Hydroxy-compounds.*

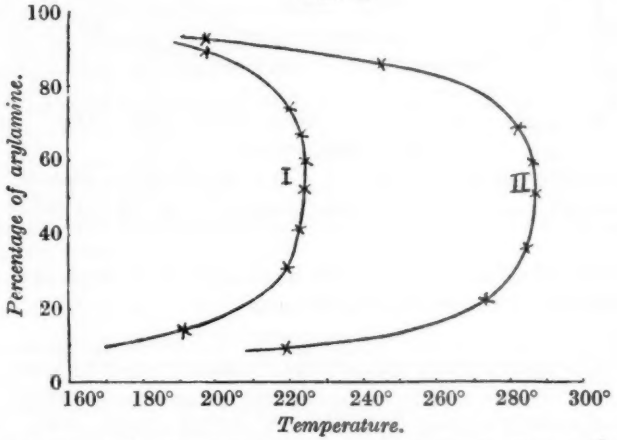
By RAM RAO PARVATIKER and BASIL CHARLES McEWEN.

THE introduction of an amino group into an aliphatic or aromatic hydrocarbon increases its solubility in water and other hydroxylic compounds (for examples, see J., 1923, **123**, 2279). *m*-Toluidine and glycerol, although not completely miscible at all temperatures,

show mutual solubility, and the complete solubility curve can be experimentally realised, the upper and the lower critical solution temperature being, respectively, 120·5° and 6·7°. Comparison with *o*- and *p*-toluidines (*loc. cit.*) shows that the mutual solubility increases with increase in the remoteness of the methyl group from the amino-group in accordance with the general principles of steric hindrance.

The miscibility of glycerol with secondary and tertiary monoamines decreases progressively with increase in the size of the alkyl groups attached to the nitrogen atom. For example, glycerol has the following upper critical solution temperatures: with monomethylaniline, 224·5°; with monoethylaniline, 273°; with dimethylaniline, 287°; and with diethylaniline, above 300°. Glycerol and benzylaniline, and glycerol and methylbenzylaniline possess, similarly, very high upper critical solution temperatures.

FIG. 1.

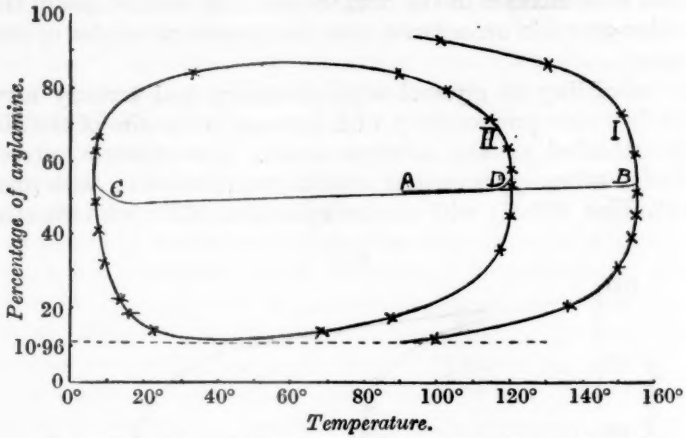


I = *Monomethylaniline + glycerol.* II = *Dimethylaniline + glycerol.*

The determinations of the solubility curves were made by Alexéev's synthetic method, as described in Part I. With *m*-toluidine and glycerol, however, it was impossible to employ the ordinary small bulb tubes for the determination of the lower half of the curve, owing to the increased viscosity of the glycerol at low temperatures. In this case, therefore, a weighing-bottle was used, provided with a rubber stopper and a stirrer so arranged as to operate without access of moisture from the air. The weighing-bottle with the synthetic mixture was first cooled in ice-water and the contents were stirred vigorously until uniform. The temperature was then allowed to rise slowly, stirring being continued, until separation into two phases

occurred. The solubility relations between glycerol and monomethylaniline and dimethylaniline, and between glycerol and *o*-toluidine and *m*-toluidine, are shown in the following tables, and in

FIG. 2.



I = o-*Toluidine* + *glycerol.* II = m-*Toluidine* + *glycerol.*

The lines AB *and* CD *give the mean composition of the two layers at each temperature for* o-*toluidine–glycerol and* m-*toluidine–glycerol, respectively.*

Figs. 1 and 2. The amount of the arylamine is, in each case, given in percentage by weight of the solution.

NHMePh ...	89·50	73·50	66·42	59·48	51·56	40·60	30·26	14·60
Soln. pt. ...	197·5°	220·0°	223·0°	224·5°	223·5°	222·5°	219·0°	190·5°
NMe_2Ph ...	92·40	86·00	68·02	58·54	50·06	35·68	21·71	9·18
Soln. pt. ...	197·5°	245·0°	282·0°	286·0°	287·0°	284·0°	273·0°	218·5°
o-$C_6H_4Me{\cdot}NH_2$	92·20		86·14		73·42	63·28		52·53
Soln. pt.	100·0°		130·0°		150·0°	154·0°		154·4°
o-$C_6H_4Me{\cdot}NH_2$	46·59		40·97		32·04	20·96		12·42
Soln. pt.	154·0°		153·0°		150·0°	137·0°		99·2°
m-$C_6H_4Me{\cdot}NH_2$ (upper half of curve)	83·23		79·23		71·58	64·30		58·68
Soln. pt.	89·0°		102·0°		113·5°	119·4°		120·5°
m-$C_6H_4Me{\cdot}NH_2$ (upper half of curve)	53·10		45·68		36·87	17·71		
Soln. pt.	120·2°		119·5°		117·5°	88·5°		
m-$C_6H_4Me{\cdot}NH_2$ (lower half of curve)	83·62		66·04		62·86	48·80		40·99
Soln. pt.	33·4°		7·8°		7·0°	6·7°		8·2°
m-$C_6H_4Me{\cdot}NH_2$ (lower half of curve)	31·40		21·68		18·72	13·99		10·96
Soln. pt.	9·2°		14·2°		16·8°	*23° and 69°		No separation

* Only slight turbidity observed.

Monomethylaniline, b. p. 190·8°/720·85 mm., $n_D^{30·0°}$ 1·5510. Dimethylaniline, b. p. 190·8°/720·85 mm., $n_D^{30·0°}$ 1·5540. *o*-Toluidine, b. p. 196·0°/721·25 mm., $n_D^{30·0°}$ 1·5653. *m*-Toluidine, b. p. 199·2°/720·85 mm., $n_D^{30·0°}$ 1·5610.

In the case of *m*-toluidine and glycerol, the law of rectilinear diameters holds fairly well, the diameter being but slightly curved for the upper portion, and somewhat more sharply curved for the lower portion of the solubility ring. It will be observed that the diameter for the upper portion of the *o*-toluidine–glycerol curve is a continuation of the diameter for the *m*-toluidine–glycerol solubility ring.

When two given liquids are each *completely* miscible with a third liquid, it cannot be stated, *a priori*, for which of the two pairs of liquids the " solution stress " has the greater value.

Information as to the relative magnitude of the mutual affinity in such cases may, however, occasionally be gained by introducing a particular substituent into the same relative position in the molecule of each of the two given liquids. Aniline and phenol, for example, are each completely miscible with glycerol. *o*-Cresol and glycerol are still miscible in all proportions, whereas *o*-toluidine and glycerol have an upper critical solution temperature of 154·4°. *m*-Cresol and glycerol are miscible in all proportions, *m*-toluidine and glycerol have an upper critical solution temperature of 120·5°. *p*-Cresol and glycerol, and *p*-toluidine and glycerol, are completely miscible.

The introduction of an alkyl group tends to decrease the solubility of carbon compounds in hydroxylic compounds, the diminution being also conditioned, as stated above, by the position taken up by the alkyl group. Since the introduction of the methyl group in the case of aniline produces a greater decrease in its miscibility with glycerol than is observed when the same group is introduced into phenol, it may be assumed that the " solution stress " between aniline and glycerol is less than between phenol and glycerol, although, in each case, it is sufficient to determine complete miscibility.

It was shown in Part II (J., 1923, **123**, 2284) that, whereas phenol and glycerol are miscible in all proportions, guaiacol and glycerol are only completely miscible below 39·5° and above 83·5°. The influence of the methoxyl group (in the ortho-position to the hydroxyl group) on the mutual solubility with glycerol may be regarded as arising from three distinct actions, *viz.*: (i) a *small increase* in mutual solubility, due to the mutual affinity between the oxygen of the methoxyl group and the oxygen in the hydroxyl groups of the glycerol; (ii) a *small decrease* in mutual solubility, due to a small amount of mutual attraction being set up between the oxygen atoms in the adjacent hydroxyl and methoxyl groups in the benzene ring, so that the remaining attraction for the oxygen atoms in the glycerol is weakened; (iii) a *decrease* in mutual solubility due to the steric hindrance exerted by the methoxyl group on the adjacent hydroxyl group in the benzene nucleus.

That the increase in mutual solubility due to (i) is very small follows from the solubility relationships which obtain between glycerol and various methoxy-derivatives of benzene. Thus glycerol and anisole have an upper critical solution temperature of 275·5°, and *o*-, *m*-, and *p*-tolyl methyl ethers have high upper critical solution temperatures. Pyrocatechol dimethyl ether (veratrole), resorcinol dimethyl ether, and quinol dimethyl ether have upper critical solution temperatures with glycerol exceeding, in each case, 240°; glycerol and pyrogallol trimethyl ether have an upper critical solution temperature of 230·5°.

The decrease in mutual solubility due to (ii) and (iii), although evidently greater than the increase due to (i) (since guaiacol and glycerol are not completely miscible between 39·5° and 83·5°), is still small, as shown by the small dimensions of the complete solubility curve of glycerol–guaiacol. That the decrease due to the mutual attraction between the oxygen atoms in the ortho-position in the benzene ring must be small was pointed out in Part II, the methyl group attached to the oxygen atom in the methoxyl group screening, to a large extent, the oxygen atom in that group, so that the decrease in mutual solubility is probably mainly the result of steric hindrance. If the methoxyl group be replaced by an ethoxyl group, the mutual solubility is considerably reduced, glycerol and pyrocatechol monoethyl ether having an upper critical solution temperature of 192·9°. The decrease in mutual solubility in this case must evidently be *mainly due to steric hindrance*, since the first and second factors will not be modified to any great extent. These conclusions are further confirmed by the fact that glycerol is miscible in all proportions with resorcinol monomethyl ether and resorcinol monoethyl ether. Glycerol is also completely miscible with quinol monomethyl ether and quinol monoethyl ether above their respective melting points (53° and 66°). Glycerol is also miscible in all proportions with orcinol and with orcinol monomethyl ether above their respective melting points (107° and 44°). On the other hand, orcinol dimethyl ether and glycerol have an upper critical solution temperature above 240°. The diethyl ethers of pyrocatechol, resorcinol, and quinol have higher upper critical solution temperatures with glycerol than the corresponding dimethyl ethers. It was observed that, at high temperatures, a certain amount of decomposition occurred both with the dimethyl and diethyl ethers, the contents of the bulb tubes becoming brown, so that the upper critical solution temperatures with glycerol could not readily be measured.

The smaller "solution stress" between aniline and glycerol than between phenol and glycerol indicates that the mutual affinity

between the oxygen atoms in the hydroxyl groups is greater than the mutual affinity between the oxygen in a hydroxyl group and the nitrogen in an amino-group. Now, *o*-anisidine and glycerol were found to have an upper critical solution temperature of 145°. In this case : (i) The *increase* in mutual solubility, due to the mutual affinity between the oxygen of the methoxyl group and the oxygen in the hydroxyl groups of the glycerol is small; (ii) the *decrease* in mutual solubility due to the mutual attraction between the nitrogen and oxygen atoms in the adjacent amino- and methoxyl groups in the benzene ring is, presumably, *less* than the decrease due to the mutual attraction between the adjacent oxygen atoms in the hydroxyl and methoxyl groups in the case of guaiacol, and is also small. The decrease in mutual solubility in this case is therefore probably mainly due to the steric hindrance exerted by the methoxyl group on the adjacent amino-group in the benzene nucleus, and, since the "solution stress" between aniline and glycerol is less than between phenol and glycerol, the upper critical solution temperature for *o*-anisidine and glycerol is higher than for guaiacol and glycerol.

It should be noted that, whereas the mutual solubility of *o*-cresol and glycerol is *greater* than that of guaiacol and glycerol, the mutual solubility of *o*-toluidine and glycerol (upper critical solution temperature 154·4°) is *less* than that of *o*-anisidine and glycerol (upper critical solution temperature 145·0°). The fact that the replacement of the methyl group in *o*-toluidine by a methoxyl group *increases* the mutual solubility with glycerol indicates that the increase in mutual solubility due to the mutual affinity between the oxygen of the methoxyl group and the oxygen in the hydroxyl groups of the glycerol is greater than the decrease in miscibility due both to the greater steric hindrance of the methoxyl group and the *small* decrease due to the mutual attraction between the nitrogen and oxygen atoms in the adjacent amino- and methoxyl groups. On the other hand, since the replacement of the methyl group in *o*-cresol by a methoxyl group *diminishes* the mutual solubility with glycerol, it must be assumed that, in this case, the *larger decrease in mutual solubility* due to the mutual attraction between the adjacent oxygen atoms in the hydroxyl and methoxyl groups in guaiacol, together with the decrease due to the greater steric hindrance of the methoxyl group, outweighs the increase due to the mutual affinity between the oxygen of the methoxyl group and the oxygen in the hydroxyl groups of the glycerol.

As might be anticipated, *p*-anisidine and glycerol are miscible in all proportions above the melting point of *p*-anisidine (57·1°).

The solubility relations between *m*-anisidine and glycerol have not

been determined, but it may be anticipated that they would lead to a closed curve of slightly smaller dimensions than the solubility ring for *m*-toluidine–glycerol.

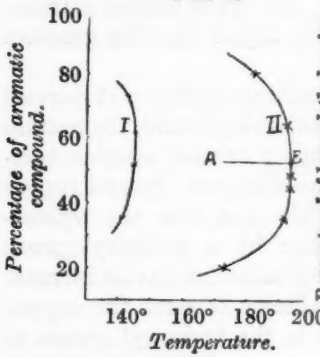
The solubility relations between *o*-anisidine and glycerol, and pyrocatechol monoethyl ether and glycerol, are shown in the following table, and in Fig. 3. The amount of the aromatic compound is, in each case, given in percentage by weight of the solution.

o-Anisidine	73·09	61·25	51·69	43·57	34·25
Soln. pt.	142·5°	145·0°	144·5°	143·0°	141·0°
Pyrocatechol monoethyl ether	79·37	63·71	48·68	44·42	35·30 20·05
Soln. pt.	183·0°	192·0°	192·8°	192·9°	191·0° 172·5°

o-Anisidine, b. p. 220°/720·85 mm., $n_D^{30·0°}$ 1·5678. Pyrocatechol monoethyl ether, b. p. 211·1°/720·85 mm., $n_D^{30·0°}$ 1·5224.

It will be observed that the diameter for the upper part of the pyrocatechol monoethyl ether–glycerol curve is a continuation of

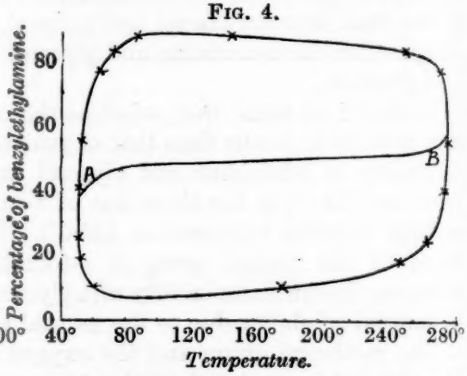
FIG. 3.



I = o-*Anisidine* + *glycerol.*
II = *Pyrocatechol monoethyl ether* + *glycerol.*

The line AB *gives the mean composition of the two layers at each temperature for pyrocatechol monoethyl ether–glycerol.*

FIG. 4.



The line AB *gives the mean composition of the two layers at each temperature.*

the diameter for the guaiacol–glycerol solubility ring shown in Part I.

Glycerol is miscible in all proportions with the lower members in the series of primary alphylamines. Thus, for example, *n*-butylamine and *iso*butylamine are completely miscible with glycerol.

When the amino-group in an aromatic compound is in the side chain, the miscibility with glycerol is greatly increased, such amino-compounds resembling the alphylamines much more closely than aniline. Benzylamine and glycerol, for example, are miscible in all proportions. Secondary benzylmethylamine and glycerol are

also miscible in all proportions, whereas monoethylaniline and glycerol have an upper critical solution temperature of 273°. In such cases a study of solubility relations would furnish important evidence as to the constitution of isomeric compounds. In the case of benzylethylamine (secondary) and glycerol, the complete solubility curve can be followed; the solubility relations between this pair of liquids are shown in the following table, and in Fig. 4. The amount of the amine is given in percentage by weight of the solution.

Benzylethylamine.	Soln. pt.	Benzylethylamine.	Soln. pt.
87·85	85° and 144°	40·06	50·1° and 279°
82·50	71 „ 253	24·48	50·0 „ 267
76·10	63 „ 277	18·07	50·0 „ 251
54·89	51 „ 281	10·14	61 „ 177

Benzylethylamine, b. p. 197·2°/720·85 mm., $n_D^{30\cdot0°}$ 1·5058.

The law of rectilinear diameters holds fairly well, the diameter being slightly curved upwards at the upper portion, and more sharply curved downwards at the lower portion of the solubility ring.

The introduction of more than one amino- or hydroxyl group, or of both hydroxyl and amino-groups, tends to increase the mutual solubility with glycerol. Thus, for example, aminoethyl alcohol and glycerol are miscible in all proportions. Similarly, solid compounds like *o*-, *m*-, and *p*-phenylenediamine, 2 : 4- and 3 : 4-tolylenediamine, *m*- and *p*-aminophenol, protocatechualdehyde, saligenin, and 2 : 4-dihydroxybenzaldehyde, are miscible with glycerol in all proportions above their respective melting points. As pointed out in Part I (*loc. cit.*), the mutual solubility with glycerol is decreased by the introduction of alkyl groups. Thus whilst protocatechualdehyde and glycerol are miscible in all proportions above the melting point of the former (153°), piperonal (m. p. 37°) and glycerol have an upper critical solution temperature of 159°; *p*-xylenol and glycerol are miscible in all proportions above the melting point of the former (74·5°), and *m*-4-xylenol and glycerol are also miscible in all proportions at the ordinary temperature, whereas carvacrol and glycerol have (like thymol and glycerol) an upper critical solution temperature above 200°; glycerol and phenylethyl alcohol (primary) have an upper critical solution temperature of 59°, whereas the upper critical solution temperature for glycerol and phenylpropyl alcohol is above 100°; glycerol and *o*-toluidine have an upper critical solution temperature of 154·4°, the upper critical solution temperature for *m*-4-xylidine and glycerol being 196·5°.

Heterocyclic compounds containing a nitrogen atom in the ring are, in general, readily miscible with glycerol: for example, pyridine, piperidine, α-picoline, and quinoline are miscible with glycerol in all proportions.

Summary.

1. The solubility relations between glycerol and members of several typical classes of carbon compounds have been examined, and it has been shown how the mutual affinity between certain atoms or groups in the molecules of a solvent and a solute gives rise to a "solution stress," tending to produce complete miscibility. Thus, the introduction of hydroxyl and amino-groups into aliphatic and aromatic hydrocarbons increases their miscibility with glycerol. The introduction of alkyl groups, however, decreases the miscibility of aliphatic and aromatic compounds with glycerol, such groups possessing but little affinity for the hydroxyl groups in the glycerol molecule.

2. The influence both of steric hindrance and of the mutual attraction between adjacent groups in carbocyclic compounds has been examined.

3. Complete solubility curves have been obtained for glycerol–guaiacol, glycerol–*m*-toluidine, and glycerol–benzylethylamine. It has been shown that the law of rectilinear diameters holds fairly well for these solubility rings, and, further, that the diameters for the upper portions of the glycerol–*o*-toluidine and glycerol–pyrocatechol monoethyl ether curves lie, respectively, on the extensions of the diameters of the solubility rings for glycerol–*m*-toluidine and glycerol–guaiacol.

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CXCIV.—*Studies in the Configuration of αα′-Dibromodibasic Acids. Part II. Derivatives of Adipic Acid.*

By Allan Willy Bernton, Harry Raymond Ing, and William Henry Perkin, jun.

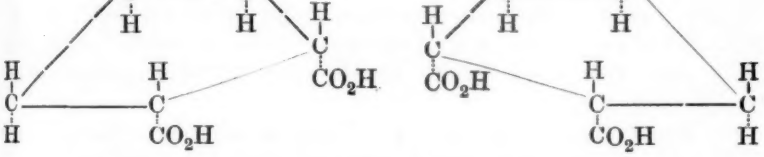
When adipic acid is brominated, it yields two isomeric αα′-dibromoadipic acids, $CO_2H{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$, called, in the previous communication, (C) and (D), which melt at 193° and 139°, respectively, and differ widely in properties. The less fusible acid (C) is sparingly soluble in water and yields a diethyl ester which melts at 67°, whereas the diethyl ester of the readily soluble acid (D) melts at 9·5° and, on distillation or on keeping, is partly converted into the ester of melting point 67°.

Attempts to establish the configuration of these acids have been

made by Rosenlew (*Ber.*, 1901, **37**, 2091), Le Sueur (J., 1908, **93**, 716), and Ingold (J., 1921, **119**, 954), whose methods are briefly sketched in Part I (J., 1921, **119**, 1393).

Rosenlew drew the conclusion that the higher-melting acid (C) is the racemic modification, whereas Le Sueur and Ingold assign this configuration to the acid of lower melting point (D). The difficulty in obtaining decisive evidence in problems of this nature depends mainly on the possibility that change of configuration may readily take place when acids of this kind are treated with strong acids or alkalis under the conditions employed in the investigations just referred to.

In order to remove this uncertainty, Perkin and Robinson (***loc. cit.***, p. 1394) caused the stable ester (m. p. 67°) of the acid (C) to react with ethyl sodiomalonate and, on hydrolysing the product, obtained a *trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid which, since it was capable of resolution into *d*- and *l*-modifications, could only be the *dl*- or racemic acid of the configuration :—



It was therefore clear, always supposing that change of configuration had not taken place during ring formation, that the dibromo-acid of melting point 193° must be *dl*-αα′-dibromoadipic acid.

In continuing this investigation, several condensations similar to those just described have been studied.

(i) The low-melting ethyl αα′-dibromoadipate interacts readily with ethyl sodiomalonate and the product is identical with that which is obtained when the higher-melting ester is employed, since on hydrolysis it yields *dl-trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid (m. p. 185°) (Condensation A).

(ii) The methyl esters of the αα′-dibromoadipic acids were prepared and obtained in two modifications, the one a crystalline substance melting at 75° (compare Stephen and Weizmann, J., 1913, **103**, 271) and the other a liquid.

The liquid methyl ester during distillation, at 170°/14 mm., is converted to the extent of about 50 per cent. into the solid isomeride, and the same change takes place very gradually at the ordinary temperature, but is much slower than that observed in the conversion of the lower-melting ethyl ester into the isomeride of higher melting

point. When these isomeric methyl esters react with methyl sodiomalonate (Condensation B), they both yield the same *methyl* cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylate* (I), a highly characteristic substance which melts at 82—84° and had not previously been described. On hydrolysis, this is converted into *dl-trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid (m. p. 185°), carbon dioxide being eliminated during the process.

$$\begin{array}{l}CH_2\cdot CH\cdot CO_2Me\\ \quad\vert\quad >C(CO_2Me)_2\\ CH_2\cdot CH\cdot CO_2Me\end{array} \rightarrow \begin{array}{l}CH_2\cdot CH\cdot CO_2H\\ \quad\vert\quad >CH\cdot CO_2H\\ CH_2\cdot CH\cdot CO_2H\end{array} \qquad \begin{array}{l}CH_2\cdot CH\cdot CO_2Et\\ \quad\vert\quad >CAc\cdot CO_2Et\\ CH_2\cdot CH\cdot CO_2Et\end{array}$$

(I.) (II.)

(iii) The solid isomeride of ethyl αα′-dibromoadipate was digested with ethyl sodioacetoacetate (Condensation C), when *ethyl* 2-*acetyl*-cyclo*pentane*-1 : 2 : 3-*tricarboxylate* (II) resulted, as was proved by the fact that it yielded *dl-trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid on hydrolysis.

(iv) In this case, the two isomerides of ethyl αα′-dibromoadipate were caused to interact with ethyl sodiobenzoylacetate (Condensation D) and again the product in each case was the same substance, namely, *ethyl* 2-*benzoyl*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, b. p. 235—242°/14 mm. On hydrolysis with methyl alcoholic potassium hydroxide, this ester yields benzoic and *dl-trans-cyclo*pentane-tricarboxylic acids.

(v) When both isomerides of methyl αα′-dibromoadipate react with methyl sodiocyanoacetate (Condensation E), *methyl* 2-*cyano*-cyclo*pentane*-1 : 2 : 3-*tricarboxylate* (III) is obtained in rhombic prisms, m. p. 83—84°, b. p. 192—196°/12 mm. Cold concentrated hydrochloric acid converts this ester into a dibasic ester (m. p. 115°), which probably has the constitution (IV).

$$\text{(III.)}\quad \begin{array}{l}CH_2\cdot CH\cdot CO_2Me\\ \quad\vert\quad >C(CN)\cdot CO_2Me\\ CH_2\cdot CH\cdot CO_2Me\end{array} \qquad \begin{array}{l}CH_2\cdot CH\cdot CO_2Me\\ \quad\vert\quad >C(CO_2H)_2,H_2O\\ CH_2\cdot CH\cdot CO_2Me\end{array} \quad \text{(IV.)}$$

If, however, the original cyano-ester is boiled with concentrated hydrochloric acid, it yields a mixture of the *cis*- and *trans*-modifications of *cyclo*pentane-1 : 2 : 3-tricarboxylic acid, melting at 170° and 185°, respectively (compare **J.**, 1921, **119**, 1399).

After these condensations had been completed, we directed our attention to the ethyl αα′-di-iodoadipates, which were first obtained by Ingold (J., 1921, **119**, 963) from the corresponding dibromoadipates by boiling in alcoholic solution with sodium iodide. These also exist in two modifications, both of which are solid and melt at 92° and 46°, respectively.

The corresponding methyl esters, which had not previously been

described, were prepared by a similar process and are characteristic substances melting at 112° and 63°, respectively. The di-iodo-ethyl esters interacted much less readily with ethyl sodiomalonate than the corresponding dibromo-esters, the greater part being recovered unchanged even after several hours' boiling on the steam-bath.

On long boiling with methyl sodiocyanoacetate, the low-melting isomeride of methyl di-iodoadipate (Condensation F) gave a small yield of the methyl 2-cyano*cyclo*pentane-1 : 2 : 3-tricarboxylate (m. p. 84°) which had been obtained from both methyl dibromo-adipates. Some unchanged methyl di-iodoadipate was, however, recovered and this proved to be the higher-melting isomeride (m. p. 112°). Consequently, the lower-melting isomeride must have been transformed into the isomeride of higher melting point during the course of the reaction.

The consideration of the results of the condensations described above seems to make it clear that the interaction of the higher-melting methyl or ethyl ester of αα′-dibromoadipic acid proceeds normally, but that, when the lower-melting esters are employed, intramolecular change into the ester of higher melting point always precedes interaction with the sodium derivative. Since this inter-change may be due to alkalinity of the sodium derivative or to the presence of sodium methoxide or ethoxide, a series of experiments on the action of varying quantities of alkali on alcoholic solutions of the isomeric αα′-dibromo- and di-iodo-adipic esters was insti-tuted. The results were surprising; for example, the liquid modi-fication of methyl αα′-dibromoadipate was quantitatively converted into the solid isomeride when mixed with sodium methoxide at −20°.

The rate of transformation depends on the amount of sodium methoxide used; thus with 2 molecular proportions, the change was complete after 2 hours, whereas with smaller quantities of the methoxide a proportionally longer time was necessary. A similar result was obtained in the case of the lower-melting modification of methyl di-iodoadipate. When an alcoholic solution of this ester was mixed with 2 molecular proportions of sodium methoxide at room temperature, the higher-melting methyl ester (m. p. 112°) began to separate immediately. These transformations may also be effected by methyl-alcoholic potassium hydroxide and, much more slowly, by methyl-alcoholic ammonia. When a large excess of alcoholic ammonia is employed, a further change takes place and the higher-melting isomerides of the dibromo- and di-iodo-esters are then converted into the corresponding diamides, m. p. 196° and 238°, respectively.

The results of this investigation show clearly that intramolecular change does not take place when the αα′-dibromoadipic ester of melting point 67° interacts with ethyl sodiomalonate and, as the resulting *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylic ester is converted, on hydrolysis, directly into *dl-trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid, it is very unlikely that intramolecular change will take place at this stage. In our opinion, therefore, the view put forward in the previous communication is the correct one, namely, that the αα′-dibromoadipic acid of melting point 193° is the *dl*- or racemic modification and that the acid of melting point 139° is consequently the *meso*-isomeride.

If this view is correct, it follows that the αα′-di-iodoadipic acids of melting point 213° and 170° are the corresponding *dl*- and *meso*-varieties.

EXPERIMENTAL.

The adipic acid and the dibromoadipates employed in this investigation were prepared according to the method of Bouveault and Locquin (*Bull. Soc. chim.*, 1908, **146**, 438) and Ingold (J., 1921, **119**, 961) respectively.

Condensation A.—The liquid isomeride of ethyl αα′-dibromoadipate (17·0 grams in alcohol, 50 c.c.) was added to ethyl sodiomalonate (from sodium, 2·3 grams, alcohol, 50 c.c., and ethyl malonate, 16·0 grams), the temperature rising to 75°. After being heated under reflux for ½ hour, the mixture, now neutral, was diluted with water and extracted with ether. After removal of ether by evaporation and of ethyl malonate by steam distillation, the residue was again treated with ether, and the extract, dried with anhydrous sodium sulphate, contained an oil, b. p. 209—211°/16 mm., which, as shown below, was ethyl *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylate (Perkin and Robinson, *loc. cit.*, p. 1397).

A portion of the oil was hydrolysed with methyl-alcoholic potassium hydroxide (25 per cent.), when the potassium salt separated at once. After 12 hours, the mixture was diluted with water, neutralised with dilute hydrochloric acid, and the alcohol evaporated. The liquid was now acidified with a considerable excess of hydrochloric acid, evaporated to dryness, and the residue extracted with acetone, the acid being more soluble in this solvent than in ether, used by Perkin and Robinson (*loc. cit.*). The residual syrup, after evaporation of the acetone, solidified almost entirely in a vacuum desiccator after a week or two. The solid, recrystallised from water, melted at 184° (Found: C = 47·6; H = 5·1. Calc. for $C_8H_{10}O_6$, C = 47·5; H = 4·9 per cent.), and comparison showed that this acid is identical with the *cyclo*pentane-1 : 2 : 3-tricarboxylic

acid which Perkin and Robinson (*loc. cit.*) had obtained from the solid isomeride of the αα′-dibromoadipate.

Amide of cyclo*Pentane*-1 : 2 : 3-*tricarboxylic Acid.*—The tribasic acid was boiled under reflux with twice the calculated quantity of thionyl chloride until it dissolved, and the excess of thionyl chloride was distilled off under reduced pressure, but the residue did not crystallise, and it was found impossible to purify the acid chloride by distillation under reduced pressure because of extensive decomposition. The crude acid chloride gradually dissolved in concentrated ammonia and after 2 hours a solid separated. After 12 hours, this was collected, washed with water, then with ether, and recrystallised from water with the aid of animal charcoal. The *triamide* of cyclo*pentane*-1 : 2 : 3-*tricarboxylic acid* was thus obtained in glistening, colourless needles, m. p. 274°, which were insoluble in alcohol, ether, or acetone (Found : N = 21·0. $C_8H_{13}O_3N_3$ requires N = 21·1 per cent.).

Condensation B.—Methyl cyclo*Pentane*-1 : 2 : 2 : 3-*tetracarboxylate.*—To methyl sodiomalonate (from sodium, 4·6 grams, methyl alcohol, 60 c.c., methyl malonate, 26·4 grams, the mixture being kept for 12 hours, to allow the sodium derivative to separate as completely as possible), the solid isomeride of methyl dibromoadipate (33·2 grams, in methyl alcohol, 100 c.c.) was added, the whole being cooled with running water for 4 hours. The solution was boiled for 3 hours and was then quite neutral. The excess of alcohol was distilled off, the methyl malonate removed by distillation in steam, and the residue extracted with ether. The dried extract on evaporation left an oil which soon crystallised. After recrystallisation from methyl alcohol and drying in a desiccator, the substance melted at 82—84°, contained no bromine, and was soluble in alcohol, acetone, benzene, chloroform, or ligroin (Found : C = 51·7; H = 5·9. $C_{13}H_{18}O_8$ requires C = 51·6; H = 6·0 per cent.). It was therefore *methyl* cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylate* (I).

The condensation of *liquid* methyl dibromoadipate with methyl sodiomalonate was performed in an exactly similar manner to Condensation B above and the same methyl *cyclo*pentanetetracarboxylate (m. p. 84°) was obtained.

Hydrolysis of Methyl cyclo*Pentane*-1 : 2 : 2 : 3-*tetracarboxylate.*—1. With methyl-alcoholic potassium hydroxide. The ester, hydrolysed in the usual way, gave a potassium salt, which, treated with hydrochloric acid and extracted with ether or acetone, yielded an oil, which solidified after some time. After recrystallisation from water, the acid melted at 184° and was *trans-cyclo*pentanetricarboxylic acid.

2. With concentrated hydrochloric acid. When the ester was

hydrolysed by boiling with concentrated hydrochloric acid for 6 hours, it gave a mixture of the *cis*- and *trans-cyclo*pentanetricarboxylic acids, melting roughly at 154° (compare Part I, p. 1399).

Condensation C.—Ethyl 2-*Acetyl*cyclo*pentane*-1 : 2 : 3-*tricarboxylate* (II).—Condensation between ethyl sodioacetoacetate and the solid isomeride of ethyl dibromoadipate was carried out in the usual manner (neutrality after 8 hours) and an oil was obtained, b. p. 181—190°/16 mm. (yield 81 per cent.) (Found: C = 56·8, 57·5; H = 7·4, 7·5. $C_{16}H_{24}O_7$ requires C = 58·5; H = 7·4 per cent.).

The ester on hydrolysis gave an oil which solidified after 3 weeks; m. p. 183°, alone or mixed with *trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid.

Condensation D.—Ethyl 2-*Benzoyl*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*.—A. The interaction between ethyl sodiobenzoylacetate (19·0 grams) and the *solid* isomeride of ethyl dibromoadipate (18·0 grams) was carried out under the usual conditions. Boiled under reflux, the product was not neutral until after 4 hours. The oil isolated in the usual manner distilled at 235—242°/14 mm. (Found: C = 63·0, 63·8; H = 6·6, 6·8. $C_{20}H_{26}O_7$ requires C = 63·5; H = 6·9 per cent.) and consisted of *ethyl* 2-*benzoyl*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*.

The ester was hydrolysed with cold methyl alcoholic potassium hydroxide and, after 24 hours, the potassium salt of *cyclo*pentane-1 : 2 : 3-tricarboxylic acid was filtered off, washed with alcohol, and dried in a desiccator (Found: K = 36·8. $C_8H_7O_6K_3$ requires K = 37·1 per cent. $C_{15}H_{11}O_7K_3$ would require K = 27·9 per cent.). The benzoyl group in position 2 had thus been eliminated during the hydrolysis.

The potassium salt was dissolved in dilute hydrochloric acid, the solution evaporated to dryness, and the mass extracted with ether. An oil was obtained which solidified after some weeks and then melted at 183°. A mixed melting point with *cyclo*pentane-1 : 2 : 3-tricarboxylic acid established identity.

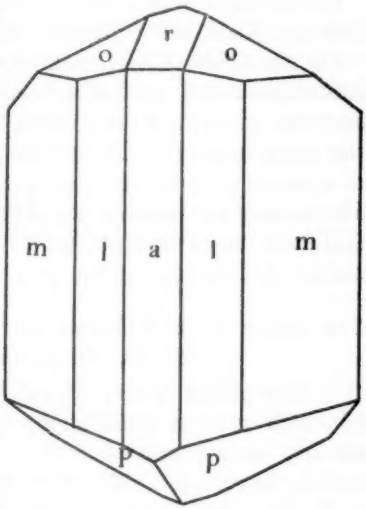
The mother-liquors from the potassium salt, on acidification, yielded benzoic acid.

B. The *liquid* isomeride of ethyl dibromoadipate, condensed with ethyl sodiobenzoylacetate, gave the same cyclic ester as had been obtained from the solid isomeride. This was shown by its boiling point and by the fact that it gave the same products on hydrolysis.

Condensation E.—Methyl 2-*Cyano*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*.—A mixture of the *solid* isomeride of methyl dibromoadipate (33·2 grams, in methyl alcohol 30 c.c.) and methyl sodiocyanoacetate (from sodium 4·6 grams, methyl alcohol 60 c.c., and

methyl cyanoacetate 19·8 grams; the sodio-derivative separated after 12 hours) was kept in a freezing mixture for 2 hours and after removal the temperature gradually rose to 30°, at which point sodium bromide began to separate. After boiling under reflux for 4 hours, the solution was neutral and was then poured into water, the dark red oil extracted with ether, the ethereal solution well washed with water, which removed the red colour, dried, and the ether evaporated. A heavy oil remained which was distilled under reduced pressure, when cyanoacetic ester (5 grams) came over first and the rest boiled at 180—198°/17 mm. This fraction (20 grams) was again distilled and boiled almost entirely at 192—196°/12 mm. and after some time the oil solidified. The solid crystallised from ether (or could be precipitated with light petroleum) in large, monoclinic crystals, m. p. 83—84° (Found: C = 53·7; H = 5·6; N = 5·2. $C_{12}H_{15}O_6N$ requires C = 53·5; H = 5·6; N = 5·2 per cent.). The substance is therefore *methyl 2-cyanocyclopentane-1:2:3-tricarboxylate* (III).

Fig. 1.



The same ester (III) was obtained when the condensation was carried out with the liquid isomeride of methyl dibromoadipate, the melting point 83—84° being again observed.

The crystals were kindly examined by Mr. T. V. Barker, who reports that they are monoclinic with $a:b:c = 1·453:1:0·530$, $\beta = 90°\ 0'$. The habit is shown in Fig. 1, the combination being *m*(100), *l*(210), *a*(100), *o*(111), *p*(111), and *r*(101), the latter sometimes failing. There are no signs of any hemihedral development, and as the reflections were rather poor, the value β may be some 6′ out. Following are the results of measurements of four crystals:

	m.	*l*.	*a*.	*o*.	*r*.	*p*.
φ.....	*34° 31′	*54° 1′	90° 0′	35° 1′	90° 0′	325° 20′
ρ.....	90 0	90 0	90 0	32 33	20 13	*32 45

Double refraction positive, extremely strong. Acute bisectrix, normal to *b*. Third mean line, approximately normal to *r*. Extinction on *m*, about 15° (through which an optic axis emerges at about 10°).

Hydrolysis with boiling concentrated hydrochloric acid converted

the cyano-ester into a solid, m. p. 154°, which proved to be a mixture of *cis*- and *trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acids.

When, however, the ester was left with concentrated hydrochloric acid at the ordinary temperature, it gradually passed into solution. The hydrochloric acid was then removed by distillation under reduced pressure at about 35°. The residual solid mass was extracted with ether, the ether evaporated, and the resulting crystals recrystallised from water. The substance, m. p. 114—115°, consisted of the *dimethyl* ester of *cyclo*pentanetetracarboxylic acid (IV) (Found: loss in a vacuum desiccator over phosphoric oxide for a week = 6·12; C = 45·9; H = 5·4. $C_{11}H_{14}O_8,1H_2O$ requires H_2O = 6·16; C = 45·2; H = 5·5 per cent.).

On titration with *N*/10-sodium hydroxide 0·1116 gram neutralised 7·60 c.c. (Calc. for a dibasic acid, 7·64 c.c.).

Condensation F.—A mixture of the lower-melting methyl di-iodoadipate and methyl sodiocyanoacetate was boiled for 4 hours and the product diluted with water and extracted with ether in the usual manner. From the first ethereal solution two fractions of crystals were isolated, m. p. 83—84° and 111—112°, respectively. The former was methyl 2-cyano*cyclo*pentane-1 : 2 : 3-tricarboxylate (III) and the latter proved to be the higher-melting isomeride of methyl di-iodoadipate (m. p. 112°) (see below).

The Esters of αα′-Dibromo- and Di-iodo-adipates and the Action of Sodium Alkyloxides on the Isomerides.

1. *The Ethyl Esters of αα′-Dibromoadipic Acid.*—These esters, of which one is a solid, m. p. 66—67°, and the other a syrup, have already been prepared both by Willstätter (*Ber.*, 1902, **35**, 2067) and by Ingold (J., 1921, **119**, 961).

II. *The Methyl Esters.*—The methyl αα′-dibromoadipate prepared by Stephen and Weizmann (J., 1913, **103**, 271) was a solid, m. p. 75°. The other isomeride is a syrup which does not seem to have been described. It was prepared as follows. Adipyl chloride, prepared from thionyl chloride and the acid, was brominated and the product poured into methyl alcohol and kept, when the solid methyl ester (m. p. 75°) gradually separated. This was filtered off, the mother-liquor poured into water, and the precipitated heavy oil, which contained some free bromine, decolorised with sodium thiosulphate and extracted with ether. The ethereal solution was then dried, evaporated, and the residue distilled under reduced pressure. The oil boiled at 169—170°/14 mm. and at 176—178°/22 mm. (Found: Br = 47·8. $C_8H_{12}O_4Br_2$ requires Br = 48·2 per cent.).

After distillation, the oil partly solidified, owing to the separation of the solid isomeride, and, when this separation was complete,

the crystals were removed by filtration, and the oil, which doubtless still contained a small quantity of the solid isomeride, was used in this condition in all subsequent experiments.

The liquid isomerides of both the ethyl and methyl dibromoadipates are partly transformed into the solid, stable isomerides by distillation under reduced pressure and also slowly on standing. The liquid methyl ester is, however, distinctly more stable than the corresponding ethyl ester, since it may be kept for nearly 2 months at the ordinary temperature without any separation of crystals.

It has now been found that this transformation also occurs when the liquid isomerides are treated with sodium ethoxide or methoxide.

The liquid isomeride of methyl αα′-dibromoadipate (16·6 grams) was dissolved in methyl alcohol and mixed with a solution of sodium (2·3 grams) in methyl alcohol. On cooling in a freezing mixture, crystals were soon deposited. They were collected (13·0 grams; m. p. 75·76°) and proved to be the *solid* isomeride of methyl αα′-dibromoadipate.

III. *The Ethyl Esters of αα′-Di-iodoadipic Acid.*—These esters, first prepared by Ingold (J., 1921, **119**, 963), melt at 46° and 92°, respectively.

IV. *The Methyl Esters of αα′-Di-iodoadipic Acid.*—The corresponding methyl esters were, however, unknown and have now been prepared in the following manner.

The acid chloride of dibromoadipic acid was poured into methyl alcohol and then diluted with water. The crude mixture of the esters was separated, dissolved in methyl alcohol, and boiled for 1 hour with excess of sodium iodide. Water was added, the oil, which gradually crystallised, dissolved in methyl alcohol, and the two isomerides were separated by fractional crystallisation, finally from light petroleum. One isomeride had m. p. 111—112° and the other 60—63°. The latter was recrystallised from acetone and then had m. p. 63° (Found: C = 22·3; H = 2·8; I = 60·5. $C_8H_{12}O_4I_2$ requires C = 22·5; H = 2·8; I = 59·6 per cent.). 100 C.c. of dry methyl alcohol dissolved 7·8 grams of the isomeride, m. p. 63°, and 0·5 gram of the isomeride, m. p. 112°. An analysis of this isomeride was not considered necessary.

The transformation of the ester of m. p. 63° into that of m. p. 112° can be demonstrated very strikingly in the following manner.

The high-melting isomeride is so very much less soluble in methyl alcohol than the low-melting ester (in the ratio 1 : 15) that the rate of transformation may be followed quantitatively by noting the

time required for the crystallisation of the high-melting isomeride after the addition of sodium methoxide to a methyl alcoholic solution of the low-melting methyl ester.

Five portions of the ester, m. p. 63° (3 grams) in methyl alcohol (45 c.c.) were treated respectively with 2, 1, ½, ¼ molecular quantities (and the fifth with a trace) of sodium, dissolved in methyl alcohol (7 c.c.); the whole was repeatedly shaken, and the time for the first appearance of crystals noted.

Mol. of Na	2	1	½	¼	Trace
Time (secs.)	almost immediate	185	325	500	2160

The same transformation also takes place in presence of alcoholic potassium hydroxide and much more gradually in presence of dilute alcoholic ammonia.

Action of Concentrated Methyl Alcoholic Ammonia on the Methyl Di-iodo- and Dibromo-adipates.—A. A well-cooled solution of methyl di-iodoadipate (m. p. 63°) in methyl alcohol was saturated with ammonia. After several days, a solid had separated which was collected, washed with water and then with ether to remove unchanged ester, and was found to consist of the *diamide* of *αα′-di-iodoadipic acid*, m. p. 233° (decomp.) (Found: I = 64·4. $C_6H_{10}O_2N_2I_2$ requires I = 64·1 per cent.). After recrystallisation from methyl alcohol, the m. p. was 238°.

B. The liquid isomeride of methyl dibromoadipate was shaken with concentrated aqueous ammonia. In about ½ hour the oil was transformed into a solid and after 4 hours this was collected and recrystallised from water. The shining, colourless crystals so obtained began to char at 180° and melted at 196°. This substance is the *diamide* of *αα′-dibromoadipic acid* (Found: N = 9·1; Br = 53·0. $C_6H_{10}O_2N_2Br_2$ requires N = 9·3; Br = 52·9 per cent.).

The *solid* isomeride, treated similarly, gave the same acid amide, m. p. 197°.

One of us (A. W. B.) wishes to express his gratitude to the Ramsay Memorial Fellowships Trust for the Swedish Ramsay Memorial Stipend for the years 1922—24, which has enabled him to take part in this work.

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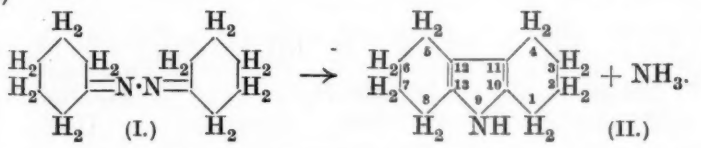
CXCV.—1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydrocarbazole and its Derivatives.*

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

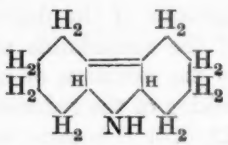
IN view of the results of our investigations of the derivatives of tetrahydrocarbazole and especially of the remarkable substances produced from its acyl derivatives by the addition of nitric acid or of hydroxyl groups to the double linking of the reduced benzene nucleus (J., 1921, **119**, 1825; 1923, **123**, 676), it became very desirable that a detailed study of the more highly reduced derivatives of carbazole should be made. The catalytic reduction of carbazole by hydrogen in presence of nickel was first investigated by Padoa and Chiaves (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 762), who claimed that this substance was thereby converted into 2 : 3-diethylindole. Von Braun and Ritter (*Ber.*, 1922, **55**, 3792) were unable to repeat these observations and found that highly purified carbazole is not reduced at 260° and under a pressure of 30 atm. of hydrogen in presence of nickel, but that the 9- or *N*-substituted derivatives such as 9-methyl- or 9-ethyl-carbazole are readily reduced under these conditions.

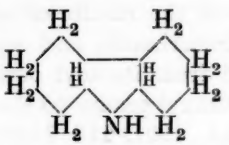
Since it did not seem possible to obtain highly reduced derivatives of carbazole in this way, and since, moreover, such a method, if successful, would give no indication of the constitution of the substances produced, we decided to have recourse to synthetical methods for the preparation of the substances we desired to investigate. Taking advantage of a process which had been employed by Robinson and Robinson (J., 1918, **113**, 639) for the preparation of tetraphenylpyrrole from phenyl benzyl ketazine, we prepared *cyclo*hexylideneazine (I) (Kishner and Bjelov, *J. Russ. Phys. Chem. Ges.*, 1911, **43**, 577; *Chem. Zentr.*, 1911, [ii], 362) from *cyclo*hexanone and hydrazine hydrate and found that this substance, on heating in tetrahydronaphthalene solution with hydrogen chloride, is converted into 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrocarbazole* (II.)



This synthesis clearly demonstrates the constitution of the octahydrocarbazole produced and there can be little doubt that the substance contains twice over the unsaturated nucleus which,

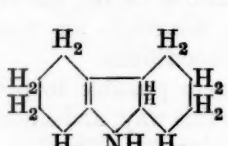
in tetrahydrocarbazole, is responsible for the characteristic properties referred to at the beginning of this communication. Long-continued reduction with tin and hydrochloric acid converts it into *decahydrocarbazole* (III), but, in the electrolytic cell, complete reduction readily takes place, and *dodecahydrocarbazole* (IV) is obtained.

(III.) 

 (IV.)

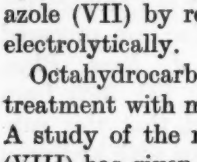
It is a remarkable fact, however, that decahydrocarbazole is quite stable towards electrolytic reduction, and is not converted into dodecahydrocarbazole under the conditions used for the preparation of the latter substance from octahydrocarbazole. This seems to indicate that this decahydrocarbazole possesses the structure represented by formula (III).

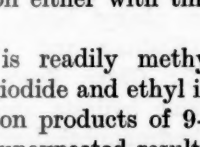
The electrolytic reduction of octahydrocarbazole clearly does not pass through this stage and is probably represented by the scheme:

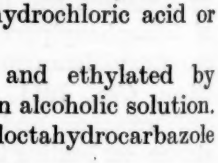
(II.) → (V.)  → (IV.)

The decahydrocarbazole of constitution (V) would be expected to yield dodecahydrocarbazole readily on reduction, since tetrahydrocarbazole (VI) is very easily converted into hexahydrocarbazole (VII) by reduction either with tin and hydrochloric acid or electrolytically.

Octahydrocarbazole is readily methylated and ethylated by treatment with methyl iodide and ethyl iodide in alcoholic solution. A study of the reduction products of 9-methyloctahydrocarbazole (VIII) has given quite unexpected results.


(VI.)

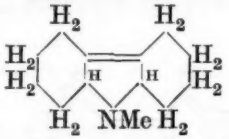

(VII.)

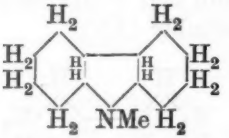

(VIII.)

By using tin and hydrochloric acid, 9-methyldecahydrocarbazole was obtained as in the case of the reduction of (II), but the electrolytic reduction of 9-methyloctahydrocarbazole also gave 9-methyl-

decahydrocarbazole and not 9-methyldodecahydrocarbazole as we had anticipated.

The constitution (IX) is assigned to 9-methyldecahydrocarbazole for reasons similar to those put forward above in the case of decahydrocarbazole. 9-*Methyldodecahydrocarbazole* (X) cannot therefore be obtained by the reduction of 9-methyloctahydrocarbazole, but it may be prepared quite readily by the direct methylation of dodecahydrocarbazole.

(IX.) 

 (X.)

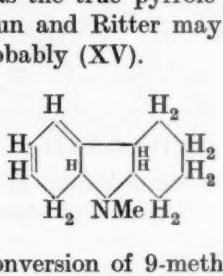
Many of the bases described in this communication are liquids, but can be identified sharply by means of their well-characterised picrates of very definite melting points.

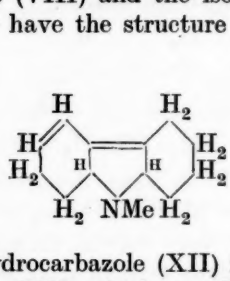
The curious behaviour of 9-methyloctahydrocarbazole on reduction made it desirable to investigate the reduction of 9-*ethyloctahydrocarbazole* (XI, corresponding with VIII). This proceeds exactly as in the case of the methyl derivative, since the same 9-ethyldecahydrocarbazole is obtained as the result of the action of tin and hydrochloric acid or of electrolytic reduction. As in the case of the corresponding 9-methyl derivative, 9-*ethyldodecahydrocarbazole* is readily obtained from dodecahydrocarbazole by the action of ethyl iodide. This investigation has a direct bearing on the work of von Braun and Ritter (*Ber.*, 1922, **55**, 3792) on the catalytic reduction of 9-methylcarbazole and of 9-ethylcarbazole with hydrogen under pressure in presence of nickel salts. These authors claim that the reduction of 9-methylcarbazole under these conditions gives rise to 9-methyltetrahydrocarbazole (XII, corresponding with VI) and 9-methyloctahydrocarbazole (VIII). The former substance was, however, not isolated, but was converted by reduction with tin and hydrochloric acid into 9-methylhexahydrocarbazole (XIII, corresponding with VII).

During the course of the present investigation, we have obtained the substance (XIII) by the electrolytic reduction of 9-methyltetrahydrocarbazole and the properties agree with those described by von Braun and Ritter.

On the other hand, the 9-methyloctahydrocarbazole (VIII) prepared by us is evidently quite a different substance from the 9-methyloctahydrocarbazole obtained by these authors as one of the reduction products of 9-methylcarbazole. The 9-methyloctahydrocarbazole of von Braun and Ritter melts at 94°, distils at 176—178°/16 mm., decomposes gradually on exposure to air, and

does not give either a crystalline picrate or a methiodide. Our 9-methyloctahydrocarbazole, obtained from octahydrocarbazole by treatment with methyl iodide, has not been obtained crystalline; it distils at 139—140°/14 mm., turns red on exposure to air, and gives a highly characteristic *picrate*, m. p. 147°, and a *methiodide*, m. p. 194°. A comparison of the methods of preparation of these two substances suggests that it is our 9-methyloctahydrocarbazole which has the true pyrrole structure (VIII) and the isomeride of von Braun and Ritter may possibly have the structure (XIV) or more probably (XV).

(XIV.) 

 (XV.)

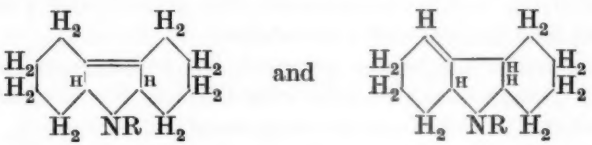
The conversion of 9-methyltetrahydrocarbazole (XII) into symmetrical 9-methyloctahydrocarbazole (VIII) which von Braun and Ritter (*loc. cit.*, p. 3794) suggest takes place during their reduction experiments seems to us to be most improbable, because we find that the reduction of (XII) to 9-methylhexahydrocarbazole (XIII) proceeds so very readily that the latter substance is probably also an intermediate stage in the catalytic reduction of (XII) to the 9-methyloctahydrocarbazole of von Braun and Ritter.

It is also highly probable that the 9-methyldecahydrocarbazole (IX) obtained by us by the reduction of our 9-methyloctahydrocarbazole, both with tin and hydrochloric acid and electrolytically, is different from that obtained by von Braun and Ritter from their isomeric 9-methyloctahydrocarbazole by reduction with tin and hydrochloric acid under similar conditions. The product of von Braun and Ritter is described as a colourless liquid, quite stable in the air, which boils at 138—139°/12 mm., gives a picrate, m. p. 162°, and a methiodide, m. p. 189°. It was not found possible to reduce it further to the corresponding dodecahydro-derivative.

Our product is also a colourless oil, quite stable in air, which distils, however, 10° lower, namely at 128°/13 mm. The *picrate* melts at 162—163°, but attempts to obtain a crystalline methiodide, which von Braun and Ritter state is formed quantitatively in the cold, were unavailing. The base also resists reduction to 9-methyldodecahydrocarbazole. Because the two bases are similar in some of their properties and both yield picrates melting at the same temperature, we were at first inclined to think that they might be identical. The difference in boiling point and the fact that the one does, and the other does not, yield a definite crystalline

methiodide is evidence against this view, and the probability that the two bases are not identical receives confirmation from the study of the corresponding ethyl derivatives. Von Braun and Ritter found that the catalytic hydrogenation of 9-ethylcarbazole proceeds apparently in an exactly similar manner to that of 9-methylcarbazole, yielding 9-ethyloctahydrocarbazole, from which, by further reduction with tin and hydrochloric acid, they obtained a 9-ethyldecahydrocarbazole. Their 9-ethyloctahydrocarbazole melts at 43°, distils at 162—163°/9 mm., turns yellow on exposure to air, and does not yield a crystalline picrate or methiodide. The 9-ethyloctahydrocarbazole prepared by us (XI, p. 1511) by the ethylation of octahydrocarbazole (II) is a liquid which distils at 166—170°/20 mm., turns yellow and then bright red on exposure to air, and very readily yields a *picrate*, m. p. 152°, and a *methiodide*, m. p. 169°. It is quite clear, therefore, that, as in the case of the methyl derivatives, these ethyl derivatives are isomeric and not identical. Turning to the corresponding higher reduction products, the 9-ethyldecahydrocarbazole of von Braun and Ritter is described as a colourless, stable liquid, boiling at 140—141°/12 mm. and yielding a picrate, m. p. 133°, and a methiodide, m. p. 176—177°. Our ethyldecahydrocarbazole is also a colourless, stable liquid and boils at 148—150°/21 mm., but the *picrate* melts at 202° and the *methiodide* at 205°. It is obvious, therefore, that the 9-ethyldecahydrocarbazoles prepared by von Braun and Ritter and by us are isomeric substances.

This indicates that the similarity in the melting points in the case of the corresponding 9-methyldecahydrocarbazoles is a coincidence and that these substances also are, as their other properties suggest, different chemical individuals. We incline to the view that the isomerism of our alkyldecahydrocarbazoles with those of von Braun and Ritter is expressed by the respective formulæ :



The results, many of them quite unexpected, obtained during our experiments on the reduction of octahydrocarbazole and its derivatives led us to include the reduction of tetrahydrocarbazole and its 9-methyl derivative in the scope of this investigation. This has resulted in the interesting observation that, in both cases, electrolytic reduction stops at the hexahydro-stage, and it would be of considerable interest to determine what changes take place

when these hexahydro-derivatives are submitted to hydrogenation in presence of nickel salts.

Experimental.

*cyclo*Hexylideneazine (I) is conveniently prepared in quantity by boiling a mixture of hydrazine hydrate (27 grams) in alcohol (300 c.c.) with *cyclo*hexanone (100 grams) for 15 minutes, removing the alcohol under diminished pressure after 12 hours, and pouring the residue into a large bulk of water. The oily azine soon solidified, and then melted at 33° and was dried in a desiccator over sulphuric acid (yield 76 per cent.).

Octahydrocarbazole (II).—*cyclo*Hexylideneazine (25 grams), dissolved in tetrahydronaphthalene (80 c.c.) at room temperature, was added during one hour to tetrahydronaphthalene (20 c.c.) at 180°, through which dry hydrogen chloride was continuously passed. The mixture rapidly became dark green and finally dark brown, and considerable quantities of ammonium chloride were formed. The mixture was then cooled, treated with hydrochloric acid (25 c.c.), the tetrahydronaphthalene removed in steam, and from the residual liquid, made alkaline with sodium hydroxide, ether extracted a dark red oil, which was distilled, the fraction, b. p. 165—170°/15 mm., readily solidifying on cooling. The octahydrocarbazole thus obtained separated from methyl alcohol containing a little water in long, thick, colourless prisms, m. p. 102° (sharp) (yield 28 per cent.) (Found : C = 82·3; H = 9·9; N = 7·9. $C_{12}H_{17}N$ requires C = 82·3; H = 9·7; N = 8·0 per cent.).

Octahydrocarbazole darkens in colour on leaving for some time exposed to the air. It dissolves readily in dilute hydrochloric acid and is reprecipitated by ammonia.

The *picrate*, greenish-yellow prisms, m. p. 140° (decomp.), was prepared from octahydrocarbazole (1·5 grams) and picric acid (2 grams) in a minimum of cold toluene.

9-*Acetyloctahydrocarbazole*, prepared by boiling octahydrocarbazole (12 grams) in acetic anhydride (50 c.c.) for 3 hours, partly separated (2·3 grams) from the clear solution, on cooling, in long, thick, colourless prisms (m. p. 73° after being washed with alcohol), but was mainly isolated by pouring the filtrate into much water, adding excess of aqueous sodium carbonate after some time and extracting the mixture with ether. The oil obtained from the dried extract readily solidified and was then crystallised from alcohol, from which 9-*acetyloctahydrocarbazole* separated in long, colourless prisms, m. p. 73° (Found : N = 6·4. $C_{14}H_{19}ON$ requires N = 6·4 per cent.).

On boiling 9-acetyloctahydrocarbazole with aqueous-alcoholic potassium hydroxide for 15 minutes and then diluting with water, octahydrocarbazole separated.

Decahydrocarbazole (III).—A mixture of octahydrocarbazole (20 grams), hydrochloric acid (180 c.c. of *d* 1·1), and granulated tin (80 grams) was boiled under reflux for 18 hours, hydrochloric acid (10 c.c. of *d* 1·16) being added at intervals of 1 hour. Ether removed from the resulting mixture, made alkaline with excess of strong aqueous sodium hydroxide, a colourless oil, which solidified almost completely on cooling. The product was pressed on porous plate and recrystallised from ether, from which *decahydrocarbazole* separated in colourless needles, m. p. 75°. The yield was good (Found : C = 81·4; H = 10·8. $C_{12}H_{19}N$ requires C = 81·4; H = 10·7 per cent.).

The *picrate*, prepared from the base and the calculated quantity of picric acid in hot methyl alcohol, separated, on cooling, in long, thick, yellow prisms, m. p. 210° (decomp.), and a further quantity was obtained by concentrating the methyl alcohol solution.

Decahydrocarbazole, dissolved in 60 per cent. sulphuric acid, was submitted to reduction in the cathode chamber of an electrolytic cell for 16 hours under the conditions described in the next section. The product obtained by making the mixture alkaline with ammonia, extracting with ether, and recrystallising from this solvent was unchanged decahydrocarbazole, m. p. 75° (picrate, m. p. 210°).

Dodecahydrocarbazole (IV).—Octahydrocarbazole (10 grams), dissolved in sulphuric acid (140 c.c. of *d* 1·5), was reduced for 16 hours in the cathode chamber of an electrolytic cell, using lead electrodes and a current of 5·5 amps. The solid precipitated from the solution, immersed in ice, by strong ammonia was removed with ether and crystallised from this solvent, *dodecahydrocarbazole* separating in colourless needles, m. p. 65°. The yield was very good (Found : C = 80·6; H = 11·5. $C_{12}H_{21}N$ requires C = 80·4; H = 11·7 per cent.). The base is readily soluble in dilute hydrochloric acid.

The *picrate*, obtained by mixing molecular quantities of dodecahydrocarbazole and picric acid in a small quantity of hot methyl alcohol, separated, on cooling, in thick, short, greenish-yellow prisms, m. p. 187° (unchanged by recrystallisation). It is much more soluble in methyl alcohol than decahydrocarbazole picrate.

9-*Methyloctahydrocarbazole* (VIII).—A solution of octahydrocarbazole (10 grams) in alcohol (40 c.c.) and methyl iodide (8·5 grams) was boiled under reflux for 6 hours, the alcohol was then removed by distillation, and the residue made alkaline with excess of aqueous sodium carbonate and extracted with ether. The ether

solution was dried with potassium carbonate, the solvent removed, and the residual, dark brown oil distilled under reduced pressure. It distilled almost completely at 139—140°/14 mm. and was collected as a pale yellow oil, which gradually turned red on exposure to the air (yield 70 per cent.) (Found: C = 82·1; H = 10·0; N = 7·3. $C_{13}H_{19}N$ requires C = 82·5; H = 10·1; N = 7·4 per cent.).

9-*Methyloctahydrocarbazole* is readily soluble in dilute hydrochloric acid and is reprecipitated by ammonia.

The *picrate*, greenish-yellow prisms, m. p. 147°, was obtained from 9-methyloctahydrocarbazole (2 grams) and picric acid (2·5 grams), dissolved in the minimal quantity of cold toluene (Found: N = 13·3. $C_{19}H_{22}O_7N_4$ requires N = 13·4 per cent.).

A solution of 9-methyloctahydrocarbazole (2·5 grams) in hot, dry toluene (30 c.c.) was warmed with methyl iodide (1·5 c.c.) for a short time; on cooling, the *methiodide* separated as a colourless solid, m. p. 194°, which was recrystallised from dry acetone (Found: I = 38·7. $C_{14}H_{22}NI$ requires I = 38·4 per cent.).

9-*Methyldecahydrocarbazole* (IX).—9-Methyloctahydrocarbazole (16 grams) was reduced with hydrochloric acid (140 c.c. of *d* 1·1) and granulated tin (64 grams) by the same method as octahydrocarbazole (p. 1509). The ethereal extract contained 9-*methyldecahydrocarbazole*, b. p. 128°/13 mm., a colourless oil which is quite stable when left in contact with the air (Found: C = 81·7; H = 11·1. $C_{13}H_{21}N$ requires C = 81·7; H = 11·0 per cent.).

9-Methyldecahydrocarbazole (7 grams), b. p. 128—129°/16 mm., was also obtained from 9-methyloctahydrocarbazole (9 grams) by the electrolytic method described on p. 1509 (Found: C = 81·8; H = 11·3 per cent.).

The base prepared by either method gave the same *picrate* on keeping the calculated amounts of the constituents in cold toluene for a few days; it separated slowly in clusters of bright yellow plates, m. p. 162—163° after a second crystallisation from toluene.

9-Methyldecahydrocarbazole could not be made to give a definite methiodide. The product was an oil, which, on standing for several days, solidified partly. A colourless solid was obtained from this on treatment with acetone, but it did not possess a definite melting point, even after recrystallisation from acetone.

9-*Methyldodecahydrocarbazole* (X).—Dodecahydrocarbazole (10 grams), prepared by the electrolytic reduction of octahydrocarbazole and subsequently purified by the recrystallisation of its picrate, was dissolved in alcohol (40 c.c.) and treated with methyl iodide (8·5 grams). The mixture was boiled for 6 hours, the alcohol removed by distillation, and the residue shaken with an excess of dilute

aqueous sodium carbonate and ether. The ether layer was dried with potassium carbonate, the solvent removed, and the remaining oil distilled under diminished pressure, when 9-*methyldodecahydrocarbazole* passed over as a colourless oil, b. p. 132°/18 mm. The yield was good (Found : C = 80·9; H = 11·8. $C_{13}H_{23}N$ requires C = 80·8; H = 11·9 per cent.).

The *picrate* separates from methyl alcohol in bright yellow prisms, m. p. 146°. A mixture of this picrate with that (m. p. 162—163°) made from a specimen of 9-methyldecahydrocarbazole obtained from the electrolytic reduction of 9-methyloctahydrocarbazole melted completely below 130°.

9-*Ethyloctahydrocarbazole* (XI).—9-Ethyloctahydrocarbazole was prepared by a process exactly similar to that employed for the preparation of 9-methyloctahydrocarbazole. It is a viscous, colourless oil, b. p. 166—170°/20 mm., which gradually turns yellow and then bright red on exposure to the air (Found : C = 82·5; H = 10·1. $C_{14}H_{21}N$ requires C = 82·8; H = 10·3 per cent.).

The *picrate* was prepared in the usual manner by mixing solutions of the constituents in cold toluene. The liquid gradually becomes dark green and the product separates, during the course of 3 days, in green needles, m. p. 152°. The *methiodide* separated readily from toluene as a colourless solid, which, after recrystallisation from dry acetone, was obtained in colourless plates, m. p. 169°.

9-*Ethyldecahydrocarbazole*.—As in the case of 9-methyldecahydrocarbazole (p. 1510), this derivative can be obtained from 9-ethyloctahydrocarbazole by reduction either with tin and hydrochloric acid or electrolytically, the conditions employed being exactly similar with both substances. 9-*Ethyldecahydrocarbazole* is a colourless liquid, quite stable in air and boiling at 148—150°/21 mm. [Found : (tin and hydrochloric acid reduction) C = 82·2; H = 11·2; (electrolytic reduction) C = 81·8; H = 11·4. $C_{14}H_{23}N$ requires C = 82·0; H = 11·2 per cent.].

The *picrate* crystallises well from hot toluene in clusters of yellow prisms, m. p. 202°, and the same picrate resulted from specimens of 9-ethyldecahydrocarbazole prepared by either of the two reduction processes. The *methiodide* separates slowly from cold toluene solution and, on recrystallisation from dry acetone, is obtained in colourless prisms, m. p. 205°.

9-*Ethyldodecahydrocarbazole*.—9-Ethyldodecahydrocarbazole was obtained by the ethylation of dodecahydrocarbazole under conditions similar to those employed for the methylation of this substance (p. 1510). It is a colourless oil, b. p. 143—145°/22 mm., and

is quite stable in air (Found: C = 81·4; H = 12·2. $C_{14}H_{25}N$ requires C = 81·2; H = 12·1 per cent.).

The *picrate* crystallises from methyl alcoholic solution in bright yellow plates, m. p. 132—133°. The *methiodide* separates readily when the cold toluene solution of the base is mixed with methyl iodide, and crystallises from dry acetone in colourless plates, m. p. 217°.

Hexahydrocarbazole (VII).—Hexahydrocarbazole can be prepared by the electrolytic reduction of tetrahydrocarbazole much more conveniently than by any of the methods previously recorded. Tetrahydrocarbazole (5 grams), dissolved in sulphuric acid (140 c.c. of *d* 1·5), was reduced in the cathode chamber of an electrolytic cell for 16 hours (see p. 1509). The solution was then made alkaline by the addition of excess of ammonia, the colourless solid collected and separated from a little inorganic matter by dissolving in ether. The extract, dried with potassium carbonate, gave, on evaporation, pure hexahydrocarbazole (m. p. 99°), the yield being practically quantitative.

9-*Methylhexahydrocarbazole* (XIII).—9-Methyltetrahydrocarbazole (15 grams), alcohol (30 c.c.), hydrochloric acid (30 c.c. of *d* 1·16), and granulated tin (30 grams) were heated together on the steam-bath under reflux for 3 hours. The hot solution was then filtered, the tin washed with a hot mixture of alcohol (10 c.c.) and hydrochloric acid (10 c.c. of *d* 1·16), and, on cooling, the clear solution deposited a colourless, crystalline tin double salt. The whole was made alkaline with excess of strong sodium hydroxide and the 9-methylhexahydrocarbazole distilled over in steam. The distillate was acidified with strong hydrochloric acid, filtered from a little unchanged 9-methyltetrahydrocarbazole, and made alkaline with excess of ammonia, the 9-methylhexahydrocarbazole extracted with ether, dried with potassium carbonate, and the solvent removed (yield 10 grams). 9-*Methylhexahydrocarbazole* distils at 144°/15 mm. and is colourless (Found: C = 83·4; H = 9·1. $C_{13}H_{17}N$ requires C = 83·4; H = 9·1 per cent.).

The *picrate* separates from hot alcohol in orange-coloured plates, m. p. 143—144° (decomp.). It was found that 9-methyltetrahydrocarbazole may be converted practically quantitatively into 9-methylhexahydrocarbazole by reduction in the electrolytic cell in the manner already described (p. 1509). The product was identified by the fact that it gave a picrate identical with that mentioned above.

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which

has defrayed part of the cost of this investigation. The authors are also grateful to Mr. R. I. E. Hall for assistance in preparing a considerable amount of the octahydrocarbazole required for these experiments, and to Mr. F. Hall for carrying out the analyses.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, April 29th*, 1924.]

CXCVI.—*Glycogen. Part I. Partial Methylation, and the Isolation of Methylated Glucoses.*

By ALEXANDER KILLEN MACBETH and JOHN MACKAY.

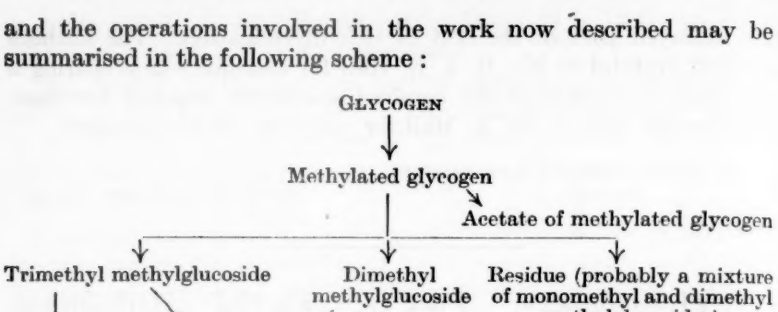
GLYCOGEN, on account of its physiological importance, has been the subject of wide research by biochemical and other workers, and the numerous publications regarding the behaviour of the compound tend to complicate the question of its constitution and make the study of the literature of the substance a somewhat laborious task. The outstanding points of chemical interest centre round the fact that the composition of the compound has been definitely established as $(C_6H_{10}O_5)_n$, and that hydrolytic agents convert the polysaccharide under certain conditions into maltose, or, on complete hydrolysis, nto glucose.

Many attempts have been made to determine the molecular weight of glycogen and so establish the value of the integer n, but the results obtained are so contradictory that it is doubtful if much reliance can be placed on any of the experimental figures.

The action of hydrolytic agents indicates a close relationship between glycogen and starch, and the points of similarity between these substances are well established. Thus Karrer (*Helv. Chim. Acta*, 1921, **4**, 994) pointed out that the action of methyl sulphate and barium or sodium hydroxide converts glycogen into a *methyloglycogen*, the properties of which are in singular agreement with those of *methylostarch*. This similarity, and the formation of corresponding compounds with sodium hydroxide by the two polysaccharides, led Karrer to express the view that starch and glycogen are fundamentally identical, the difference in their behaviour towards iodine and water being accounted for by the presence of impurities in the starch. This opinion, however, seems to be adequately refuted by the work of Pringsheim and Lassmann (*Ber.*, 1922, **55**, [*B*], 1409).

The present research was undertaken with the object of investig ating the nature of the basal unit of glycogen by examining the products obtained on hydrolysis of the methylated polysaccharide,

and the operations involved in the work now described may be summarised in the following scheme:


GLYCOGEN
Methylated glycogen
Acetate of methylated glycogen
Trimethyl methylglucoside
Dimethyl methylglucoside
Residue (probably a mixture of monomethyl and dimethyl methylglucosides)
2 : 3 : 5 : 6-Tetramethyl methylglucoside
2 : 3 : 5 : 6-Tetramethyl glucose
2 : 3 : 6-Trimethyl glucose
Dimethyl glucose
Dimethyl ester of dimethyl-saccharic acid.

The alkylation of glycogen was accomplished by the repeated action of methyl sulphate in presence of sodium hydroxide, a method which may safely be applied in view of Pflüger's observation (*Pflüger's Archiv*, 1902, **92**, 81) that the polysaccharide may be boiled for many hours with a 36 per cent. solution of potassium hydroxide without being destroyed. After several methylations, a methylated glycogen was obtained having a methoxyl content of about 37 per cent. This has evidently passed the stage in which two of the hydroxyl groups are methylated (32 per cent. of methoxyl), but is short of complete alkylation of the three hydroxyls (45 per cent. of methoxyl): the product may therefore be expected to yield a mixture of dimethyl and trimethyl glucose on hydrolysis, and in practice this expectation was realised.

The methylated glycogen referred to above is very resistant to further alkylation, possibly owing to steric hindrance effects or to the physical condition of the compound. We incline to the latter view, for the solubility of the methylated glycogen in alkali decreased considerably as alkylation proceeded, and in further methylations it was extremely difficult to prevent it from separating from solution. The steric hindrance view, however, would seem to be supported by the difficulty of alkylation by methyl iodide and silver oxide. The fact that the partly methylated glycogen contains residual free hydroxyl up to the limit of three such groups is readily proved by the action of acetylating agents. An acetylated product may be readily obtained, the analysis of which shows that the polysaccharide contains only three hydroxyl groups, some of which are methylated and the remainder acetylated. Observations of a similar difficulty

in methylation have been recorded by Irvine and Macdonald (*Rep. Brit. Assoc.*, Section B, Hull meeting), and by Pringsheim and Persch (*Ber.*, 1921, **54**, [*B*], 3162; 1922, **55**, [*B*], 1425) in the case of tetra-amylose and diamylose.

By continued action of methyl sulphate and sodium hydroxide the alkylation of glycogen may be carried further than the 37 per cent. stage, and a product has now been obtained which contains some 40 per cent. of methoxyl. The further investigation of the action is proceeding and the results will be embodied in a later communication. In this connexion it may be mentioned that starch has been completely methylated in this laboratory (Irvine and Macdonald, private communication).

The trimethyl glucose obtained on hydrolysis of methylated glycogen (37 per cent. of methoxyl) is identical with that from methylated cellulose, cellobiose, and lactose. The derivation of this sugar from the different sources, and its characteristic properties, have been summarised by Irvine and Hirst (J., 1922, **121**, 1213), and on examination of the results given in the experimental part of this paper the identity of the trimethyl glucose described with the 2 : 3 : 6-compound will be evident.

The dimethyl methylglucoside obtained in the work and also dimethyl glucose derived from it by hydrolysis with hydrochloric acid, were isolated only as clear, viscous syrups, which did not crystallise even when kept for several months. The sugar forms no osazone and therefore it must be presumed that the 2-position is methylated. On oxidation, it gives rise to a dimethyl dimethylsaccharate, hence the compound is probably either 2 : 3- or 2 : 5-dimethyl glucose. From the following comparison between our compound and Irvine and Scott's (J., 1913, **103**, 575) dimethyl glucose (probably the 2 : 3-compound), it would appear that the dimethyl glucose derived from glycogen is the 2 : 5-compound.

Dimethyl glucose from glycogen.	Dimethyl glucose of Irvine and Scott.
Syrup.	Crystalline solid : α-form, m. p. 85—87°. β-form, m. p. 108—110°.
$[\alpha]_D$ equilibrium value in water, +55·4°.	$[\alpha]_D$ equilibrium value in water, +64·4°.
Methyl glucoside is a syrup.	Methyl glucoside is crystalline, m. p. 80—82°.
$[\alpha]_D$ in acetone, +80·15°.	$[\alpha]_D$ in acetone, +143·49°.

The formation of 2 : 5-dimethyl glucose in the methylation experiments was altogether unexpected, as no trace of a trimethyl glucose other than the 2 : 3 : 6-compound had been detected. Accordingly, it does not seem advisable to assign the 2 : 5-structure definitely to

the dimethyl glucose isolated in the work until such time as the whole question of the constitution of the isomeric dimethyl sugars has been further studied.

Irvine and Macdonald (*loc. cit.*), in discussing the attachment of nitrogen and phosphorus to the starch molecule, conclude that these elements form part of the polymerised aggregate. On treatment of a partly methylated nitrogenous starch with methyl iodide and silver oxide, the whole of the material was precipitated as an insoluble additive compound with silver iodide; and on this account they are of the opinion that the nitrogen-containing constituent is definitely polymerised to the starch unit, as otherwise only partial precipitation is to be expected. Similar considerations do not hold in the case of glycogen, for specimens not specially purified, which had a fairly high nitrogen content, lost their nitrogen during the early methylations; and, moreover, it seems to be fairly well established that glycogen may be purified by purely physical methods and thus obtained nitrogen-free.

The close agreement between the behaviour of starch and glycogen on methylation, and the similarity of the products obtained on hydrolysis of the methylated compounds seem clearly to indicate that the polysaccharides are both built up from the same basal unit. The various formulæ proposed for starch may therefore be considered applicable in the case of glycogen, and in this connexion the structures suggested by Irvine and Macdonald are of special interest. Karrer (*Helv. Chim. Acta*, 1923, **6**, 402) has taken exception to the units proposed, as he finds that by the action of acetyl bromide at 0° soluble starch is converted into acetobromomaltose, without the formation of any appreciable quantity of acetobromoglucose. A triamylose formula therefore seems to be excluded, for such a structure may be expected to lead to the formation of acetobromomaltose and acetobromoglucose in the ratio of 2 : 1. The objection is readily met by modifying Irvine's formula so as to include six hexose residues in the polysaccharide unit. The structures, however, still remain open to the objection that no 2 : 3 : 5-trimethyl glucose has up to the present been detected in the hydrolytic products obtained from methylated glycogen; and the units under consideration imply the formation of this sugar in addition to the 2 : 3 : 6-isomeride, in the ratio of approximately 2 : 1.

Experimental.

Methylation of Glycogen.—Rigorously purified material was employed in the early experiments, but the glycogen used in later work was not specially purified and contained nitrogen, moisture, and glucose (reducing sugars, expressed as glucose, = about 0·96

per cent.); nitrogenous compounds were removed as volatile bases during methylation and reducing sugars were eliminated by extraction with ether at different stages of the process. Alkylation was effected with methyl sulphate and sodium hydroxide in the usual way. After three methylations, the product, which was freed from methylated glucoses by extraction with ether, did not reduce Fehling's solution, and contained no nitrogen [OMe = 26·7 per cent.; $[\alpha]_D$ in chloroform = + 152·5° (c = 1·70)]. The yield was only 20 grams, the loss in the initial methylations being mainly due to the impurities in the original material. Owing to the difficulty experienced in keeping the carbohydrate in solution during further methylations, methyl alcohol was added to the reaction mixture, and after one such treatment the product isolated had the composition of a dimethylglycogen; yield 19·5 grams, $[\alpha]_D$ in chloroform = + 166° (c = 1·476) [Found: C = 50·51; H = 7·41; OMe = 31·1. $C_6H_8O_3(OMe)_2$ requires C = 50·5; H = 7·3; OMe = 32·6 per cent.]. There is no proof that the product was a homogeneous compound; the agreement may be due to compensation, the product containing glycogen methylated above and below the dimethyl stage.

Two more methylations in presence of methyl alcohol, followed by extraction as described above, gave a product (19 grams) which, after treatment with ether to remove impurities, showed OMe 36·4 per cent. and $[\alpha]_D$, in chloroform, + 179·83° (c = 1·51). This methyloglycogen was an almost white solid, soluble in alcohol, methyl iodide, or chloroform, and insoluble in ether. It contained no reducing sugars, and gave negative tests for nitrogen (Found: C = 50·98; H = 7·7. Calc. for a 36 per cent. methoxy-compound, C = 51·16; H = 7·5 per cent.).

Further action of the methylating agents increased the methoxyl content very slowly, and therefore the product was hydrolysed.

Hydrolysis of Partly Methylated Glycogen.—Two methods were employed, (*a*) heating with acid methyl alcohol under pressure, yielding a trimethyl methylglucoside which did not crystallise on keeping, and (*b*) heating with the same reagent under reflux, leading to the isolation of the crystalline compound.

(*a*) A solution of 8 grams of methyloglycogen (OMe = *ca.* 37 per cent.) in 180 c.c. of dry methyl alcohol containing 1 per cent. of hydrogen chloride was heated in sealed tubes at 130° for 72 hours. After cooling, the acid was neutralised with silver carbonate, the solution boiled for a short time with norit and filtered, the solvent was removed, and the residual syrup extracted with ether. The clear syrup (7·4 grams) remaining after filtration and removal of the ether was distilled, three fractions being collected: A, 1·52 grams,

b. p. 119—122°/0·15 mm.; B, 1·11 grams, b. p. 135—138°/0·65 mm.; C, 2·87 grams, b. p. 142—145°/0·20 mm.: residue 1·6 grams. Corresponding results were obtained in the distillations in various experiments.

Fraction A, on redistillation, had the same b. p., n_D 1·4584, $[\alpha]_D$, in chloroform, + 57·9° (c = 1·52), and did not crystallise on standing (Found: C = 50·72; H = 8·61; OMe = 51·8. Trimethyl methyl glucoside requires C = 50·85; H = 8·48; OMe = 52·6 per cent.).

Fraction B, having OMe = 45·8 per cent. and n_D 1·4614, was evidently a transition fraction consisting of dimethyl and trimethyl methylglucosides.

Fraction C, after redistillation, had b. p. 142—145°/0·2 mm., n_D 1·4736, and $[\alpha]_D$, in acetone, + 80·15° (c = 1·78) (Found: C = 48·4; H = 8·28; OMe = 40·8. Dimethyl methylglucoside requires C = 48·65; H = 8·11; OMe = 41·9 per cent.).

Residue.—The residue after distillation, a very viscous, brown syrup (OMe = 34·8 per cent., average value), was hydrolysed (1·5 grams) with boiling 6 per cent. hydrochloric acid (100 c.c.) for 3½ hours. From the solution neutralised with barium carbonate, after the removal of solvent, chloroform extracted 1·1 grams of a brown glass containing 24·9 per cent. of methoxyl. This value indicates that the initial syrup was composed mainly of the lower methylated methylglucosides, for according as it consisted of a mixture of monomethyl and dimethyl methylglucosides or of a depolymerised methylated glycogen, it should have given on hydrolysis the corresponding sugars having methoxyl values of 16—30 per cent. and about 32 per cent., respectively.

(*b*) A solution of 8 grams of methylated glycogen (37 per cent. of methoxyl) in 200 c.c. of dry methyl alcohol containing 1·5 per cent. of hydrogen chloride was, after the addition of a little norit, heated under reflux on a water-bath. The course of the reaction was followed polarimetrically, and after 7½ hours the mixture was cooled, neutralised with silver carbonate, and worked up in the usual way. Upwards of 7 grams of a clear syrup were thus obtained, which on distillation (Gaede pump) gave three fractions similar to those described above. Analyses of the fractions were in good agreement with the results already recorded, and crystallisation of the first fraction commenced within 12 hours and was almost complete after 3 days. The product was drained on porous tile and recrystallised from light petroleum, the glucoside being obtained in long, colourless needles, m. p. 54°. The melting point may be raised a few degrees by recrystallisation, values as high as 60° having been recorded. It is not depressed when the glucoside is mixed with

authentic specimens of 2 : 3 : 6-trimethyl methylglucoside derived from starch.

Examination of the Trimethyl Methylglucoside (Fraction A).

(*a*) *Butylene-oxide Linking.*—To prove the presence of this linking, 1 gram of the syrup was twice methylated with methyl iodide and freshly-prepared silver oxide, and the product distilled. The clear syrup obtained, b. p. 110—112°/0·7 mm., n_D 1·4460, OMe = 61·3 per cent. (2 : 3 : 5 : 6-tetramethyl methylglucoside requires n_D 1·4460; OMe = 62 per cent.), was hydrolysed with boiling 8 per cent. hydrochloric acid for 45 minutes, a little norit being present and from the solution, neutralised with barium carbonate, chloroform removed a colourless syrup which, on nucleation with 2 : 3 : 5 : 6-tetramethyl glucose, soon crystallised. The crystals melted at 76°, and at 94° after repeated crystallisation from light petroleum. The sugar showed the usual mutarotation of tetramethyl glucose in water, the optical value changing from + 92·4° to + 83·3°. The original trimethyl methylglucoside therefore belongs to the butylene-oxide series.

(*b*) *Hydrolysis to* 2 : 3 : 6-*Trimethyl Glucose.*—A solution of 2·5 grams of the syrupy glucoside in 100 c.c. of 6 per cent. hydrochloric acid was boiled under reflux in presence of norit until the rotation became constant. Hydrolysis was complete after 5 hours. The solution was cooled, neutralised with barium carbonate, most of the barium chloride precipitated with an excess of alcohol, and, after filtration and removal of the solvent under diminished pressure, the residual syrup was extracted with ether and the extract dried with anhydrous sodium sulphate. The syrup obtained on evaporation of the ether soon crystallised, and the product was recrystallised from the same solvent. After one crystallisation the fine, white needles melted at 74°, but this value was increased, after two further crystallisations, to 107—110° (Found: C = 48·53; H = 7·91; OMe = 41. Trimethyl glucose requires C = 48·65; H = 8·11; OMe = 41·9 per cent.). The specific rotation in methyl alcohol (c = 1·424), initially + 75°, attained the constant value + 67·84° after 5 days.

The constants determined for the trimethyl glucose isolated from glycogen are in good agreement with those already established for the crystalline 2 : 3 : 6-trimethyl glucose isolated from cellobiose, cellulose, and starch. The melting points of mixtures of our compound with specimens of the trimethyl glucose isolated from the above sources showed no depression, and therefore the compound obtained from glycogen is evidently the 2 : 3 : 6-compound also, of the butylene-oxide type.

Examination of the Dimethyl Methylglucoside (Fraction C).

(*a*) *Butylene-oxide Linking.*—The glucoside was shown to belong to the butylene-oxide series by its conversion on methylation with methyl iodide and silver oxide into tetramethyl methylglucoside. Subsequent hydrolysis of this product in the usual way led to the isolation of 2 : 3 : 5 : 6-tetramethyl glucose.

(*b*) *Hydrolysis to Dimethyl Glucose.*—A solution ($[\alpha]_D$ + 52·5°) of 2·7 grams of the dimethyl methylglucoside in 150 c.c. of 6 per cent. hydrochloric acid was boiled under reflux until the rotation became constant (after 150 minutes; $[\alpha]_D$ + 41·4°, or corrected for dimethyl glucose, + 44·1°). The solution was then neutralised with barium carbonate and worked up as described in the previous hydrolysis. The residue was extracted with boiling acetone, and the dimethyl glucose remained as a very viscous syrup on removal of the solvent; yield 2·1 grams. In a separate experiment, 2·9 grams of the glucoside gave 2·3 grams of the dimethyl sugar. The equilibrium value for the sugar in water was $[\alpha]_D$ + 55·4° (c = 1·128) [Found : OMe = 28·9. $C_6H_{10}O_4(OMe)_2$ requires OMe = 29·8 per cent.].

Examination of the Dimethyl Glucose.

(*a*) *Non-formation of Osazone.*—No difficultly soluble crystalline derivative was obtained when the sugar was treated with phenylhydrazine under the conditions for osazone formation. The 2-position in the sugar chain would therefore appear to be methylated. Apparently the sugar does not form a condensation product with acetone, for no change was observed in the specific rotation of a solution containing 2 per cent. of hydrogen chloride.

(*b*) *Oxidation.*—The preceding observations indicate that the dimethyl glucose is either the 2 : 3- or the 2 : 5-compound, and this view is supported by the results obtained on oxidation and subsequent esterification. Under these conditions the sugars should be converted into a dimethyl dimethylsaccharate, whereas, if the 6-position is methylated, a dimethyl monomethylsaccharate should be formed. Two grams of the dimethyl glucose were heated with 30 c.c. of nitric acid (*d* 1·2), at 80° until brown fumes appeared and at 64—65° until the evolution ceased. The oxidation was then arrested by dilution with water, and the nitric acid removed by distillation under reduced pressure, water and, later, methyl alcohol being constantly added, until 2½ litres and 1½ litres, respectively, of distillate had been collected. All solvent was then removed under reduced pressure, and the residual syrup (which was distinctly acid to litmus) esterified by boiling under reflux for 6 hours with 100 grams of methyl alcohol containing 2 per cent. of hydrogen chloride.

After cooling, the solution was neutralised with silver carbonate, filtered, and the solvent distilled off. The brown syrup (1·8 grams) obtained by extraction with chloroform was distilled under greatly diminished pressure. A fraction (0·5 gram) of pale yellow syrup was obtained which on analysis gave results in agreement with a dimethyl dimethylsaccharate; n_D 1·4630, b. p. approximately 125°/0·2 mm. [Found : C = 44·6; H = 6·97; OMe = 45·5. $C_6H_6O_4(OMe)_4$ requires C = 45·1; H = 6·77; OMe = 46·6 per cent.].

Acetylation of Methylated Glycogen.—A solution of 2·5 grams of methylated glycogen (OMe = 36—37 per cent.) and 4 grams of fused sodium acetate in 30 c.c. of acetic anhydride was boiled under reflux for 90 minutes and the excess acetic anhydride removed under reduced pressure. Chloroform extracted from the residue a solid acetyl derivative, $[\alpha]_D + 191·2°$ in chloroform ($c = 1·558$), which contained the theoretical quantity (14·3 per cent.) of acetyl, estimated by titrating a solution in standard alkali after 24 hours' keeping.

We wish to thank the Carnegie Research Trust for a scholarship which enabled one of us to take part in this work : we are also indebted to Dr. E. L. Hirst and Dr. J. Macdonald for specimens of 2 : 3 : 6-trimethyl glucose, and to Principal Irvine for his interest in the work.

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CXCVII.—*The First Law of Photochemistry.*

By MURIEL CATHARINE CANNING CHAPMAN.

THE majority of researchers in photochemistry have assumed that the amount of chemical change in a given system effected by light of a specified wave-length is proportional to the light absorbed. Although this is a fundamental principle of the greatest importance, the experimental evidence for its universal validity is not conclusive. Draper (*Lon. Ed. Dub. Phil. Mag.*, 1843, **23**, 401), in the case of the photochemical interaction of hydrogen and chlorine, found that the above relation was at least approximately true, but its accuracy has been challenged by Baly and Barker (J., 1921, **119**, 653), who observed that the rate of combination of hydrogen and chlorine increases with the intensity of the light more rapidly than Draper's law requires. The experiments described below are a re-examination of this question.

Experimental.

The apparatus used was similar to that described in a recent paper by the author (J., 1923, **123**, 3062). In addition to observing all the precautions therein mentioned, the insolation vessel, after it had been filled with the mixture of chlorine and hydrogen, was heated in a bath of hot water at 96° for several hours. The usual tests for destructible inhibitive impurities were applied, and in all cases their absence was demonstrated.

The following method of varying the intensity of the light was adopted. Light from a 1000-candle-power lamp passed through six horizontal rectangular slits of equal size in a brass plate, and then through two white translucent glass plates, placed in contact with the brass plate. The light by its passage through the two glass plates was effectively scattered. The slits could be covered by shutters so that the insolation vessel could be illuminated by the light which emerged from one or more of them.

The method of determining the relative rates of formation of hydrogen chloride was the same as that described in the paper referred to above, that is, the fall of pressure in the insolation vessel occasioned by an exposure to light for a definite interval of time was measured with the precautions necessary to secure accuracy, and the rate was taken to be proportional to the quotient of the observed fall of pressure and the total time of exposure. By adopting this procedure we clearly assume that the interval of time which elapses between the beginning of the exposure to light and the attainment of the steady state is negligibly small in comparison with the total duration of the exposure.

That such an assumption is a very close approximation to the truth can be shown by observing the movement of the index of a Bunsen actinometer of suitable construction, which contains electrolytic gas free from destructible inhibitive impurities. The forward movement of the index during the first minute is not less than the movement during any subsequent minute. However, a more conclusive proof of the legitimacy of the assumption is furnished by the results of the experiments described below. The actinometer was exposed to the light for exactly 1 minute and left in the dark for $\frac{1}{4}$ hour, the actinometer being meanwhile shaken at intervals in order to bring its gaseous and liquid contents into equilibrium. This procedure was repeated several times and the total combination thus occasioned was compared with the combination which was brought about by a single exposure to the light lasting the same number of minutes. The results of three experiments conducted in this way are recorded below.

No. of expt.	No. of slits open.	Time of exposure in minutes.	No. of exposures.	Fall of pressure in cm. of mercury.
1 (*a*)	6	5	1	0·406
(*b*)	6	1	5	0·412
(*c*)	6	5	1	0·408
2 (*a*)	2	10	1	0·276
(*b*)	2	1	10	0·269
(*c*)	2	10	1	0·274
3 (*a*)	2	1	10	0·278
(*b*)	2	10	1	0·286

It is obvious that the discrepancy between the results of the continuous and the discontinuous exposures is sufficiently small to amply justify us in neglecting to consider the effect of any initial period of gradually increasing rate of combination in the subsequently recorded results.

In the first series of observations on the effect of varying the intensity of the light the rate of combination of the gases in the actinometer was measured (1) with all slits open, (2) with the two top slits open, (3) with the two middle slits open, (4) with the two bottom slits open, (5) with all six slits open again. About ¾ hour elapsed between two consecutive observations. The sum of all the measurements made with a pair of slits open was then compared with the mean of the two measurements made with all six slits open. If the total quantity of hydrogen chloride formed is comparatively small, it is evident that if the two quantities compared are equal the rate of combination must be proportional to the intensity of the light to the first order of small quantities, whether or no the amount of light admitted to the insolation vessel from each pair of slits is the same.

It will be seen that by this method of procedure the introduction of fresh electrolytic gas during the series of observations is avoided. The addition of new gas to a highly sensitive mixture is undesirable, since it would contain an unknown amount of oxygen, and therefore diminish the sensitiveness to an extent which could not be estimated.

A second series of observations was made in which the effect of the light from a pair of slits was compared with that of the light from the separate slits. From these observations and those previously made, the effect of reducing the intensity of the light to one-sixth of its original value could be deduced.

The experimental results are tabulated below. The slits taken in order are distinguished by the letters A, B, C, D, E, F.

Preliminary experiments, using slits cut in cardboard.

Initial pressure of electrolytic gas = 39·45 cm. of mercury.

About 0·1 per cent. of oxygen was present.

No. of expt.	No. of slits open.	Time of exposure in minutes.	Fall of pressure in cm. of mercury.	Rate of combn. per hour.	
I. *a*	3	5	0·496	5·952	Mean of rates in I*a* and I*c* = 5·724.
b	1 (A)	15	0·454	1·816	Sum of rates in I*b*, I*c*, and I*d* = 5·768.
c	1 (B)	15	0·527	2·108	Ratio of intensities = 1 : 3.
d	1 (C)	15	0·461	1·844	Corresponding ratio of rates of combination = 1 : 2·98.
e	3	5	0·458	5·496	
II. *a*	3	10	0·292	1·752	Intensity of light reduced.
b	1 (A)	30	0·285	0·570	Mean of rates in II*a* and II*c* = 1·677.
c	1 (B)	30	0·331	0·662	Sum of rates in II*b*, II*c*, and II*d* = 1·756.
d	1 (C)	30	0·262	0·524	Ratio of intensities = 1 : 3.
e	3	10	0·267	1·602	Corresponding ratio of rates of combination = 1 : 2·87.

Experiments using slits in brass plate.
Initial pressure of electrolytic gas = 44·5 cm. of mercury.
Very little oxygen was present.

No. of expt.	No. of slits open.	Time of exposure in minutes.	Fall of pressure in cm. of mercury.	Rate of combn. per hour.	
III. *a*	6	6	0·438	4·380	Mean of rates in III*a* and III*c* = 4·23.
b	2 (A, B.)	18	0·450	1·500	Sum of rates in III*b*, III*c*, and III*d* = 4·487.
c	2 (C, D)	18	0·438	1·460	Ratio of intensities = 1 : 3.
d	2 (E, F)	18	0·458	1·527	Corresponding ratio of rates of combination = 1 : 2·83.
e	6	6	0·408	4·080	
IV. *a*	2 (C, D)	18	0·450	1·500	Mean of rates in IV*a* and IV*d* = 1·455.
b	1 (C)	36	0·438	0·730	Sum of rates in IV*b* and IV*c* = 1·487.
c	1 (D)	36	0·454	0·757	Ratio of intensities = 1 : 2.
d	2 (C, D)	18	0·423	1·410	Corresponding ratio of rates of combination = 1 : 1·96.
V. *a*	2 (A, B)	18	0·454	1·513	Mean of rates in V*a* and V*d* = 1·520.
b	1 (A)	36	0·496	0·827	Sum of rates in V*b* and V*c* = 1·610.
c	1 (B)	36	0·470	0·783	Ratio of intensities = 1 : 2.
d	2 (A, B)	18	0·458	1·527	Corresponding ratio of rates of combination = 1 : 1·89.
VI. *a*	2 (E, F)	18	0·462	1·540	Mean of rates in VI*a* and VI*d* = 1·500.
b	1 (E)	36	0·473	0·788	Sum of rates in VI*b* and VI*c* = 1·531.
c	1 (F)	36	0·446	0·743	Ratio of intensities = 1 : 2.
d	2 (E, F)	18	0·438	1·460	Corresponding ratio of rates of combination = 1 : 1·96.

No. of expt.	No. of slits open.	Time of exposure in minutes.	Fall of pressure in cm. of mercury.	Rate of combn. per hour.	
VII. *a*	6	6	0·412	4·120	Mean of rates in VII*a* and VII*e* = 3·885.
b	2 (A, B)	18	0·415	1·383	Sum of rates in VII*b*, VII*c*, and VII*d* = 4·090.
c	2 (C, D)	18	0·408	1·360	Ratio of intensities = 1 : 3.
d	2 (E, F)	18	0·404	1·347	Corresponding ratio of rates of combination = 1 : 2·85.
e	6	6	0·365	3·650	
VIII. *a*	2 (C, D)	18	0·408	1·360	Mean of rates in VIII*a* and VIII*d* = 1·315.
b	1 (C)	36	0·404	0·673	Sum of rates in VIII*b* and VIII*c* = 1·320.
c	1 (D)	36	0·388	0·647	Ratio of intensities = 1 : 2.
d	2 (C, D)	18	0·381	1·270	Corresponding ratio of rates of combination = 1 : 1·99.
IX. *a*	6	6	0·338	3·380	Mean of rates in IX*a* and IX*e* = 3·345.
b	2 (A, B)	18	0·354	1·180	Sum of rates in IX*b*, IX*c*, and IX*d* = 3·567.
c	2 (C, D)	18	0·354	1·180	Ratio of intensities = 1 : 3.
d	2 (E, F)	18	0·362	1·207	Corresponding ratio of rates of combination = 1 : 2·81.
e	6	6	0·331	3·310	
X. *a*	3 (A, B, C)	12	0·296	1·480	Mean of rates in X*a* and X*e* = 1·452.
b	1 (A)	36	0·315	0·525	Sum of rates in X*b*, X*c*, and X*d* = 1·561.
c	1 (B)	36	0·308	0·513	Ratio of intensities = 1 : 3.
d	1 (C)	36	0·312	0·523	Corresponding ratio of rates of combination = 1 : 2·80.
e	3 (A, B, C)	12	0·285	1·425	

From experiment III and experiments IV—VI it can be deduced that when the ratio of intensities = 1 : 6 the corresponding ratio of the rates of combination = 1 : 5·49.

From experiments VII and VIII it can be deduced that when the ratio of intensities = 1 : 6 the corresponding ratio of the rates of combination = 1 : 5·67.

On the other hand, from two selected points on the curve published by Baly and Barker I estimate that when the intensity of the light was increased in the ratio of 1 : 6 the rate of combination increased in the ratio of 1 : 10.

It will be seen that these results do not confirm those obtained by Baly and Barker. On the contrary, the rate of combination of electrolytic gas appears to increase with the intensity of the light rather *less* rapidly than is required by Draper's law. In order to test this conclusion under somewhat different conditions, the following experiments were performed. In these, since the results of experiments III—X demonstrated that the amount of light issuing from each slit was practically the same, the rate of

combination occasioned by opening six slits was directly compared with that of the combination induced by opening the two middle slits.

No. of expt.	No. of slits open.	Time of exposure in minutes.	Fall of pressure in cm. of mercury.	Rate of combn. per hour.	
XI. *a*	6	60	0·362	0·362	Intensity of light much reduced.
b	2 (C, D)	180	0·367	0·122	Ratio of intensities = 1 : 3. Corresponding ratio of rates of combination = 1 : 2·97.
XII.**a*	6	10	0·269	1·614	Gas mixture contained only 3% H_2.
b	2 (C, D)	30	0·215	0·430	Mean of rates in XII*a* and XII*c* = 1·269.
c	6	10	0·154	0·924	Ratio of intensities = 1 : 3. Corresponding ratio of rates of combination = 1 : 2·95.
XIII. *a*	6	20	0·312	0·936	Gas mixture contained only 20% Cl_2.
b	2 (C, D)	60	0·305	0·305	Mean of rates in XIII*a* and XIII*c* = 0·906.
c	6	20	0·292	0·876	Ratio of intensities = 1 : 3. Corresponding ratio of rates of combination = 1 : 2·97.

* It is obvious that much reliance cannot be placed on the result of this experiment owing to the large—although unavoidable—fall in the proportion of hydrogen contained in the mixture during the course of the experiment.

The deviation from Draper's law, already mentioned, may be ascribed either to the temporary reduction in the pressure of the water vapour occasioned by the formation of hydrogen chloride or to a slight inhibitive effect of the hydrogen chloride itself. The former cause appears to be the more probable.

In the author's opinion, the results of the research demonstrate almost conclusively, even in the case of the photochemical change which exhibits the greatest departure from Einstein's law of photochemical equivalence, the validity of Draper's law.

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CXCVIII.—*The Decomposition of Ethylene Bromide by Potassium Iodide and Sodium Iodide Solutions.*

By T. S. PATTERSON and JOHN ROBERTSON.

FROM remarks in two papers by Berthelot (*Compt. rend.*, 1857, **44**, 1249; 1862, **54**, 517) it would appear that at a temperature of

275° ethylene bromide, water, and potassium iodide yield ethane. The reaction is seldom mentioned in the literature, and such allusions as there are are contradictory and given without references. We have found that there is no need to heat to 275°; on gentle boiling, considerable quantities of gas are easily produced, iodine being liberated. On examining the reaction quantitatively we found the following as typical of a number of experiments. 5·643 Grams of ethylene bromide heated with 19 grams of potassium iodide and 20 c.c. of water gave 602 c.c. of gas absorbable by bromine water, which, on analysis, gave results agreeing with those of ethylene, and a small residue, probably impurity, which was neither ethane nor hydrogen. The reaction is thus presumably represented by the equation $C_2H_4Br_2 + 2KI = C_2H_4 + 2KBr + I_2$. The iodine liberated corresponded to a yield of 607·4 c.c. of ethylene. A minute quantity of ethylene iodide was also formed, doubtless as a secondary product. With a concentrated solution of potassium iodide, ethylene was given off more rapidly than with a dilute solution. The reaction proceeded further with excess of ethylene bromide than with excess of potassium iodide, but potassium chloride and potassium bromide had no effect upon ethylene bromide. Ethylene chloride, ethylene iodide, and acetylene tetrabromide, boiled with aqueous solution of potassium iodide, gave only a very small yield of ethylene. Propylene bromide gave propylene, but with greater difficulty. In alcoholic or acetone solution there is little reaction between potassium iodide and ethylene bromide, but in alcohol, and especially in acetone, in which it is easily soluble, sodium iodide reacts readily, even in the cold, both with ethylene bromide and with ethylene iodide, ethylene being rapidly evolved. With ethylene chloride there is no perceptible action, and only a slight action with acetylene tetrabromide. The gases were tested in all cases for acetylene, but with negative results.

In the experiments with sodium iodide and acetone the formation of a crystalline compound was noticed and on further investigation we found that by mixing acetone solutions of sodium iodide and of iodine a substance crystallising in faintly green needles is very easily formed. This compound melts at about 74°, cannot be recrystallised from any solvent tried, decomposes very rapidly in air, but seems to be quite stable in an atmosphere of acetone. We are at present investigating this point.

UNIVERSITY OF GLASGOW. [*Received, April 2nd,* 1924.]

CXCIX.—*Tautomerism of Dyads. Part II. Acetylene and its Halogen Derivatives.*

By Edith Hilda Ingold (Usherwood).

In a paper read before the British Association (see *Chem. and Ind.*, 1923, **42**, 1246), the suggestion was made that acetylene would show a type of tautomerism analogous to that of hydrocyanic acid, and that the gas, although consisting mainly of HC:CH, contains in equilibrium a very small amount of an isomeride, *iso*acetylene, CH_2:C. The suggestion was based partly on the formal similarity between acetylene and hydrocyanic acid,

$$[H]C{:}N \rightleftharpoons C{:}N[H] \qquad [H]C{:}CH \rightleftharpoons C{:}CH[H]$$

(mobile hydrogen distinguished thus : [H])

partly, also, on the evidence obtained by Nef (*Annalen*, 1897, **298**, 332; 1899, **308**, 325) and Lawrie (*Amer. Chem. J.*, 1906, **36**, 489) of the existence of halogeno*iso*acetylenes, such as $C{:}CBr_2$; but chiefly on the evidence afforded by the appearance, in the case of acetylene, of certain properties (such as capacity for forming metallic derivatives) which in other cases always arise simultaneously with tautomeric mobility. It is of interest from these three points of view that acetylene (and also its monohalogen derivatives) has now been shown to exhibit tautomeric mobility of the kind suggested.

Acetylene.

Two kinds of evidence have been brought to bear on the case of acetylene itself. In the first place, an examination by the thermodynamic method for the detection of tautomeric equilibria in very mobile systems, which was applied to hydrocyanic acid in Part I of this series (Usherwood, J., 1922, **121**, 1604), has given indications of the existence in gaseous acetylene of a mobile equilibrium between individuals related to one another similarly to the two forms of hydrocyanic acid; that is to say, the concentration of one isomeride very greatly exceeds that of the other, and the scarcer constituent possesses the greater internal energy. An estimate of the proportion in which the scarce constituent occurs at any given temperature cannot be made in this case for lack of a necessary thermochemical datum (for the theory of the calculation, see Part I), but from a comparison of the specific heat curve with that previously obtained, and on chemical grounds also (see below), it is plain that near the ordinary temperature the unstable form must represent only a very small fraction of 1 per cent. of the whole, although at 200—300° its concentration begins to be appreciable.

In the second place, a study of the behaviour of the gas on oxidation under very cautiously regulated conditions has shown that the isomeride $C{:}CH_2$ actually exists, in minute amounts, in gaseous acetylene.

The analogy with *iso*nitriles, the primary oxidation products of which are their direct additive compounds with oxygen (carbimides),

$$R{\cdot}N{:}C + O \longrightarrow R{\cdot}N{:}C{:}O$$

(Gautier, *Annalen*, 1869, **147**, 313), suggests that the first oxidation products of all substances possessing the *iso*acetylene structure should be ketens :

$$R_2C{:}C + O \longrightarrow R_2C{:}C{:}O.$$

That this is so for the halogeno*iso*acetylenes is evident from the work of Nef (*loc. cit.*) and Lawrie (*loc. cit.*). Thus in the case of the dibromo-compound, the *iso*-structure of which has been established by the oxidation of its hydrogen-iodide additive product by means of nitric acid to dibromoacetic acid (Lawrie, *loc. cit.*),

$$CBr_2{:}C \longrightarrow CBr_2{:}CHI \longrightarrow CHBr_2{\cdot}CO_2H,$$

the initial oxidation product is dibromoketen (which undergoes further oxidation to bromine and carbon monoxide), for if the oxidation is carried out in presence of ethyl alcohol, ethyl dibromoacetate is produced :

$$CBr_2{:}C{:}O + EtOH \longrightarrow CHBr_2{\cdot}CO_2Et.$$

There can be little doubt, therefore, that the production of a keten on regulated oxidation is a characteristic property of the *iso*acetylene structure.

By cautious oxidation of acetylene, Bone and Andrew (J., 1905, **87**, 1232) established the simultaneous production of formaldehyde and carbon monoxide at an early stage of the reaction. This result has been confirmed, but, probably on account of the small concentration of the active isomeride, great difficulty was experienced in detecting still earlier products. Ultimately, however, by regulating the reaction as described in the experimental portion of this paper, the production of keten was proved.

The mechanism of the reaction up to Bone and Andrew's earliest detected products may therefore be represented as follows :

$$CH_2{:}C \xrightarrow[O]{} CH_2{:}C{:}O \xrightarrow[O]{} CH_2\!-\!\overset{O}{\diagdown\diagup}\!-CO \longrightarrow CH_2O + CO,$$

and it is interesting to note that in certain of Bone and Andrew's

experiments (*loc. cit.*) a solid by-product was obtained which appeared to be a polymeride of the keten-oxide figured above.

Bone and Andrew realised that the formaldehyde and carbon monoxide could not be the primary products, but must arise from some oxygenated two-carbon substance, and to express this idea in definite form they proposed the scheme:

$$HC{:}CH \longrightarrow HO{\cdot}C{:}C{\cdot}OH \longrightarrow CH_2O + CO.$$

It is difficult to believe, however, that in a gaseous oxidation oxygen would thus insert itself between carbon and hydrogen, leaving the triple bond unattacked, and the mechanism now proposed not only seems intrinsically more reasonable, but also receives support from the experiments now described.

The subsequent oxidation of the formaldehyde to formic acid, and of this to carbonic acid, represented by Bone and Andrew thus,

$$H{\cdot}CHO \longrightarrow HO{\cdot}CHO. \qquad H{\cdot}CO_2H \longrightarrow HO{\cdot}CO_2H,$$

are, for similar reasons, better regarded as oxygen-additive reactions * involving the reactive forms (compare Baly, J., 1922, **121**, 1080) of formaldehyde and formic acid, respectively:

$$\begin{matrix} H \\ OH \end{matrix}\!\!>\!C \longrightarrow \begin{matrix} H \\ OH \end{matrix}\!\!>\!C{:}O. \qquad \begin{matrix} HO \\ HO \end{matrix}\!\!>\!C \longrightarrow \begin{matrix} OH \\ OH \end{matrix}\!\!>\!C{:}O.$$

They are then uniform with the oxidation of *iso*acetylenes to ketens, of *iso*nitriles to carbimides, and of carbon monoxide to carbon dioxide.

It is probable that, especially above 300°, the mechanism of the oxidation is complicated by the direct interaction of oxygen and the normal acetylene structure.

* Nevertheless, the addition of an atom of oxygen in all these gaseous oxidations must be the result of a two-stage process, since molecular oxygen is the real reagent:

$$CRR' \xrightarrow{O_2} CRR'{:}O{:}O \xrightarrow{CRR'} 2CRR'{:}O.$$

Since the mechanism assumed for the oxidation of formaldehyde and formic acid must hold for other aldehydes, the view expressed by the equations given above receives confirmation from the fact that a peroxide almost certainly intervenes in the auto-oxidation of benzaldehyde:

$$CHPh{:}O \rightleftharpoons CPh(OH) \longrightarrow CPh(OH){:}O{:}O \longrightarrow CPh(OH){:}O.$$

Similarly, the conversion of keten into its oxide (glycollolactone) is presumably a two-stage process; this is in agreement with the isolation by Staudinger of "moloxides," $\begin{matrix} CR_2 \\ | \\ CO \end{matrix}\!\!>\!O{:}O$, as well as "oxides," $\begin{matrix} CR_2 \\ | \\ CO \end{matrix}\!\!>\!O$, from the auto-oxidation products of many of the ketens.

The Halogen Acetylenes.

The contrast between the sweet-smelling, harmless hydrocarbon and its evil-smelling, very poisonous, explosive and spontaneously inflammable halogen derivatives is very marked. Nef regarded the latter properties as characteristic of the *iso*acetylene structure, and he assigned this constitution both to the mono- and di-halogen derivatives. It is the author's purpose to show, however, that whilst the dihalogen derivatives are undoubtedly static *iso*acetylenes possessing the structure assigned to them by Nef ($C{:}CBr_2$; $C{:}CI_2$ *), the monohalogen compounds are tautomeric substances possessing normal acetylene as well as *iso*acetylene phases. Thus chloroacetylene must be represented :

$$[H]C{:}CCl \rightleftharpoons C{:}CCl[H].$$

Chloroacetylene, since its discovery by Wallach (*Annalen*, 1880, **203**, 88), has been but little investigated. It has the foregoing typical properties, and the evolution of energy attending its oxidation is such that its aqueous solution generates ozone and glows in the dark. Bromoacetylene has similar characteristics (Ssabanajev, *J. Russ. Phys. Chem. Ges.*, 1885, **17**, 175; Nef, *Annalen*, 1897, **298**, 359).

It is suggested that these properties may be explained if, unlike acetylene itself, chloroacetylene and bromoacetylene possess each a large *iso*-phase at the ordinary temperature. This was readily proved in the case of chloroacetylene, for on treatment with iodine a chlorodi-iodoethylene was obtained which evidently had its two iodine atoms attached to the same carbon atom, alkalis transforming it into di-iodoacetylene, the constitution of which has been proved by its conversion into the dibromodi-iodoethylene which Lawrie (*loc. cit.*) has brought into connexion with dibromoacetic acid :

$$CHCl{:}C \xrightarrow[+I_2]{} CHCl{:}CI_2 \xrightarrow[-HCl]{} C{:}CI_2 \xrightarrow[+Br_2]{} CBr_2{:}CI_2.$$

Equally plain evidence has been obtained that chloroacetylene is capable of reacting as though it had the normal acetylene structure, bright illumination converting it into *s*-trichlorobenzene, a type of reaction characteristic of triply-linked structures.

Finally, the tautomeric nature of the substance was shown in an experiment on the addition of hypobromous acid : two additive products, chloroacetic acid and chlorodibromoacetaldehyde, were formed, one derived from each of the two isomerides originally in equilibrium.

* $C{:}CCl_2$ is not known (see p. 1532).

$$\begin{array}{l} CCl[H]{:}C \xrightarrow{(HOBr)} [CHCl{:}CBr{\cdot}OH \rightleftharpoons CH_2Cl{\cdot}COBr] \xrightarrow{(H_2O)} CH_2Cl{\cdot}CO_2H \\ \quad\Downarrow \\ CCl{:}C[H] \xrightarrow{(HOBr)} [CClBr{:}CH{\cdot}OH \rightleftharpoons CHClBr{\cdot}CHO] \xrightarrow{(HOBr)} CClBr_2{\cdot}CHO \end{array}$$

Whilst evidence of the same general character applies to monobromoacetylene, which displays its dual chemical character, for instance, by yielding, on the one hand a di-iodide, $CHBr{:}CI_2$, convertible into di-iodo*iso*acetylene, $C{:}CI_2$, and, on the other, *s*-tribromobenzene by polymerisation, a marked contrast becomes apparent on turning to the dihalogenoacetylenes. For example, these compounds show not the slightest tendency to pass into halogenated benzenes, although, as the formation of hexamethylbenzene from dimethylacetylene shows, there is no inherent difficulty about the production of hexa-substituted benzenes from di-substituted acetylenes having the necessary triple linking. In fact, whilst the *iso*acetylene constitution of the dihalogen compounds has been proved in many ways, there is, so far as the author is aware, no fact in the chemistry of these substances which necessitates reference to the normal structures, $CBr{:}CBr$ and $CI{:}CI$. It must therefore be concluded that in contrast to the tautomeric monohalogen compounds, the dihalogen derivatives are *iso*acetylenes rendered static by the absence of a mobile hydrogen atom.

The halogeno- and dihalogeno-acetylenes exemplify the rule that a tautomeric system, blocked by a halogen atom, tends to acquire the hydrogen necessary for tautomerism by reduction in presence of alkali,

$$R{-}Br + KOH = R{-}[H] + KOBr$$
([H] = mobile hydrogen atom).

Di-iodo*iso*acetylene is comparatively stable, but, as Lawrie noticed (*loc. cit.*), dibromo*iso*acetylene becomes spontaneously reduced to the monobromo-compound,

$$C{:}CBr_2 + KOH \longrightarrow C{:}C[H]Br + KOBr,$$

and all the author's attempts to prepare the unknown static dichloro-*iso*acetylene have resulted in the production of the tautomeric monochloro-compound, spontaneous reduction of the dichloro-derivative having apparently occurred at the moment of its formation.*

* Gotts and Hunter (this vol., p. 442), in support of Macbeth's contention that the lability of halogen atoms is the result of induced positive polarity, point out that, since the electro-negative nature of the halogens is in the order Cl>Br>I, the order of reactivity by induction should be I>Br>Cl; which is true for the dihalogenodinitromethanes. That the reactivity of the dihalogenoacetylenes is in the opposite order illustrates the danger of generalising from an isolated class of examples.

From the preceding account, it is evident that acetylene derivatives may be classified as (i) static acetylenes possessing the normal structure (examples: $CH_3{\cdot}C{:}CI$; $CH_3{\cdot}C{:}C{\cdot}CH_3$), (ii) tautomeric acetylenes (examples: $CH{:}CH \rightleftharpoons C{:}CH_2$; $CH{:}CCl \rightleftharpoons C{:}CHCl$), and (iii) static *iso*acetylenes (examples: $C{:}CBr_2$; $C{:}CI_2$); and there seems to be no clear reason why pairs of isomerides belonging to classes (i) and (iii) may not be found. The author hopes to provide further evidence bearing on this point in the near future.

Experimental.

(A) *The Ratio of the Specific Heats of Acetylene between* 0° *and* 200°.

Acetylene was prepared from calcium carbide, purified by Mathews' method of washing with acid copper sulphate solution and chromium trioxide dissolved in sulphuric acid (*J. Amer. Chem. Soc.*, 1899, **22**, 107), and dried by passing over phosphoric oxide.

The apparatus and the method of working were essentially those employed in the case of hydrocyanic acid (*loc. cit.*).

Corrections for deviations from the gas laws were made by means of the critical data and Nernst's formula ("Theoretical Chemistry," 4th ed., p. 245), based on D. Berthelot's equation of state:

$$\gamma_{C_2H_2} = \gamma_{air} \cdot \phi_{C_2H_2} \cdot \{(\lambda/2)_{C_2H_2}/(\lambda/2)_{air}\}^2 \cdot M_{C_2H_2}/M_{air}$$

where

$$\phi = 1 - \frac{9}{64} \cdot \frac{p}{p_c} \cdot \frac{T_c}{T}\left\{1 - 6\left(\frac{T_c}{T}\right)^2\right\};$$

λ represents the wave-length, M the molecular weight of either gas, p and T the pressure and absolute temperature of the acetylene, and p_c and T_c the corresponding critical constants. Air was used as the standard gas, and the values $\gamma_{air} = 1{\cdot}403$ and $M_{air} = 28{\cdot}98$ were employed. McIntosh's values of the critical data for acetylene were taken, viz. $T_c = 309{\cdot}5°$ abs. and $p_c = 61{\cdot}6$ atms. (*J. Physical Chem.*, 1907, **11**, 306; *J. Amer. Chem. Soc.*, 1914, **36**, 737).

Several experiments were made at each of the temperatures given in the following table, where the numbers recorded for the pitch of the nodes represent the reduced results of a large number of determinations:

Temp.	15°	100°	140°	182°	197°	210°
$\lambda/2$ for air (cms.)	6·084	6·935	7·295	7·650	7·768	7·862
$\lambda/2$ for C_2H_2 (cms.)	5·968	6·763	7·079	7·366	7·462	7·536

Since, in the final set of experiments, the same exciting rod and tube were used throughout, it was found convenient to plot the

values of $\lambda/2$ for air and for acetylene, and to calculate the values of γ, given below, from the smoothed curves.

Temp.	0°	25°	50°	75°	100°
γ	1·231	1·227	1·218	1·210	1·204
Temp.	125°	150°	175°	200°	
γ	1·195	1·185	1·174	1·163	

(B) *The Regulated Oxidation of Acetylene.*

A brief account of these experiments has been given in the introduction, and since the results in general confirm those of Bone and Andrew, all that is necessary here is a description of the conditions in which the formation of keten was observed.

The essential conditions for this are: (i) the ratio of acetylene to oxygen should be very great, of the order of 500 : 1; (ii) a suitably devised "hot-and-cold" tube should be used in order to "fix" enough of the unstable products for detection; (iii) the gases should be pure and dry; (iv) the temperature should be low, and contact material absent.

A long coil of wide glass tubing, sealed to a capillary tube, was immersed in a bath at 290—300° so that the capillary tube was wholly outside this, and separated from it by asbestos packing. In this way, a mixture of the purified acetylene and dry air (about 100 : 1 by vol.), streaming at a carefully adjusted speed through the apparatus, was maintained at the temperature of the bath for a considerable time to undergo the early stages of interaction, and was then cooled extremely quickly to minimise decomposition of the products.

The presence of keten in the issuing gas was proved by the following experiments:

(i) The gas was passed into a solution of 0·1 gram of *p*-bromoaniline in about 20 c.c. of benzene for 1½ hours, the unchanged base was then removed with 2*N*-hydrochloric acid, the benzene evaporated, and the viscous residue treated for 5 minutes with 20 per cent. hydrochloric acid in order to remove the bases $CH_2(NH{\cdot}C_6H_4Br)_2$ and $CH_2{:}N{\cdot}C_6H_4Br$ formed from the *p*-bromoaniline and the formaldehyde produced by the further oxidation of the keten. The insoluble residue, after crystallisation from carbon tetrachloride, melted at 164·5—166°, and was identified as *p*-bromoacetanilide by direct comparison and a mixed melting point determination with an authentic specimen.

(ii) In a similar experiment with *p*-toluidine, the gas passing for 8½ hours, the product, after twice crystallising from carbon tetrachloride, melted at 147—149°, and was identified as aceto-*p*-toluidide by direct comparison, by a mixed melting-point determination with

an authentic specimen, and by analysis (Found: C = 72·3; H = 7·7. Calc., C = 72·5; H = 7·4 per cent.).

The formation of these substituted acetamides, which were obtained only under the conditions described, proves the occurrence of keten in the oxidised gas.

(C) *Monochloroacetylene.*

Preparation.—The mercury compound was prepared by Hofmann and Kirmreuther's method (*Ber.*, 1909, **42**, 4234), modified in detail. A mixture of 50 grams of dichloroethylene and 150 c.c. of alcohol was run in a fine stream into a rapidly churned solution of 100 grams of mercuric chloride, 45 grams of sodium cyanide, and 100 grams of potassium hydroxide in 800 c.c. of water. After 1 hour, the precipitate was collected, washed with water and a little alcohol, and crystallised from chloroform, from which the mercury salt (50 grams), m. p. 186°, separated (Found: Cl = 21·9. Calc., Cl = 22·2 per cent.).

Ten grams of the mercury compound were suspended in 500 c.c. of a solution containing 10 grams of sodium cyanide and 5 grams of potassium hydroxide, and the air was displaced by nitrogen, as the gas is spontaneously inflammable in air. The mixture was warmed on a water-bath, and the gas evolved was led through a reflux condenser, and dried by sulphuric acid and phosphoric oxide. For analysis, it was converted into the silver salt by leading it into ammoniacal silver nitrate (Found: Ag = 64·4; Cl = 21·2. Calc., Ag = 64·5; Cl = 21·2 per cent.). The silver salt is extremely explosive, detonating with great violence, even when handled with caution, not only in the dry state, but also when moist, and even under water, quantities as small as 0·1 gram causing considerable damage.

Properties and Liquefaction.—In addition to the properties mentioned, monochloroacetylene possesses an extremely nauseating odour reminiscent both of yellow phosphorus and of carbylamines; its inhalation, even in traces, produces very unpleasant symptoms. It is also treacherously explosive, and may detonate during manipulation for very small cause. When the gas, diluted with nitrogen, was passed through a tube cooled in solid carbon dioxide and ether, a colourless liquid formed, which began to boil at − 32° to − 30° and then exploded with extreme violence.

Action of Iodine: Formation of Di-iodoisoacetylene.—The gas, diluted with nitrogen, was passed for 1 hour into 500 c.c. of well-cooled benzene, to which 25 grams of iodine were added gradually to keep pace with the decoloration. After keeping for 4 hours, the solution was shaken with aqueous sodium hydroxide to remove

the iodine, dried with calcium chloride, and the benzene distilled off through a fractionating column. The residue was distilled under reduced pressure, when the main bulk boiled constantly at 118°/35 mm. (Found: C = 7·9; H = 0·7. C_2HClI_2 requires C = 7·7; H = 0·3 per cent.). When the oil was treated with cold alcoholic potash, cold alcoholic sodium ethoxide, or hot alcoholic sodium phenoxide, di-iodo*iso*acetylene was obtained, which, crystallised from light petroleum, melted at 78° (Found: I = 90·9. Calc., I = 91·4 per cent.).

Action of Light: Formation of s-*Trichlorobenzene.*—The gas, diluted with nitrogen, was passed over a 100-watt lamp in such a way that it was both heated and illuminated. The grey fog that appeared in the apparatus gradually settled on the glass surfaces as a greasy solid, which was collected. The tarry mass was boiled with 95 per cent. alcohol and animal charcoal, and the filtered solution evaporated to dryness. The yellow residue was rubbed with cold chloroform. The insoluble portion decomposed at about 290°, and could not be obtained crystalline. On evaporating the chloroform, the soluble portion was deposited in well-defined crystals, which separated from ethyl acetate–ligroin in needles, m. p. 63°. It was identified by its properties and analysis as *s*-trichlorobenzene (Found: C = 40·0; H = 1·8. Calc., C = 39·7; H = 1·7 per cent.).

On repeating the experiment, a violent explosion occurred when the light was switched on.

Action of Hypochlorous Acid: Formation of Chloroacetic Acid, Chloral Hydrate, and Dichloroacetaldehyde Hydrate.—A solution of chloroacetylene, made by passing the gas from 20 grams of the mercury salt into 200 c.c. of water at 0°, was mixed with 30 c.c. of a 30 per cent. solution of sodium hypochlorite to which 500 c.c. of saturated boric acid solution had been added. After standing for several days, the solution was acidified with 5 per cent. sulphuric acid, and extracted with a large volume of ether. The ethereal solution was concentrated without drying, and washed with sodium hydrogen carbonate solution. The washings were then acidified and re-extracted with ether. The acid product so obtained, after removal of ether, solidified on keeping in a desiccator. It was crystallised from a mixture of ether and ligroin, and identified as chloroacetic acid by odour, melting point (61—62°), mixed melting point with an authentic specimen, and titration (Found: M = 94·9. Calc., M = 94·5). On removing the ether from the neutral extract, a solid was obtained, which was fractionally crystallised from carbon disulphide, two fractions of the same melting point but differing considerably in solubility being obtained. The less soluble

portion was identified as chloral hydrate by melting point (57°), mixed melting point with an authentic specimen, and by conversion on rubbing with solutions of sodium carbonate and hydroxylamine hydrochloride into the hydroxylamine derivative, $CCl_3 \cdot CH(OH) \cdot NH \cdot OH$, m. p. 98° (compare Hantzsch, *Ber.*, 1892, **25**, 702). The more soluble fraction, m. p. 56—57°, was identified as dichloroacetaldehyde hydrate (recorded m. p. 55—56°) by conversion with hot semicarbazide acetate solution into glyoxal-semicarbazone (Found: C = 27·8; H = 4·8. Calc., C = 27·9; H = 4·6 per cent.).

Action of Hypobromous Acid: Formation of Chloroacetic Acid and Chlorodibromoacetaldehyde Hydrate.—Chloroacetylene was passed for 1 hour into a solution of hypobromous acid (about 5 per cent.), prepared from bromine, water, and mercuric oxide by Dancer's method (*Annalen*, 1863, **125**, 242), kept at 0°. After standing for some days, the solution was extracted with ether and worked up as in the previous experiment on the addition of hypochlorous acid. The acid product was identified as chloroacetic acid by melting point (61—62°), mixed melting point with an authentic specimen, and titration (Found: M = 95·2. Calc., M = 94·5). The neutral product, after crystallisation from carbon disulphide, melted at 51—52°, and was identified as chlorodibromoacetaldehyde hydrate (Found: C = 9·8; H = 1·2. Calc., C = 9·4; H = 1·2 per cent.).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CC.—*Titanous Salts as Reducing Agents.*

By EDMUND KNECHT.

IN previous communications (*Ber.*, 1903, **36**, 166, 1549; 1904, **37**, 3475; 1905, **38**, 3318; 1907, **40**, 3819; P., 1910, 229; *J. Soc. Dyers and Col.*, 1906, **22**, 165, 330; 1908, **24**, 68; 1909, **25**, 135, 160; 1915, **34**, 94, 205, 241; 1920, **36**, 215; *J. Soc. Chem. Ind.*, 1908, **27**, 434; 1909, **28**, 189; 1915, **34**, 126), it has been shown that the powerful reducing action of the titanous salts can be utilised with advantage in the quantitative determination of a number of inorganic and organic substances by volumetric methods, details of which are described. The present work contains an account of further observations and of some new applications of

standardised titanous chloride solution in the volumetric analysis of certain organic compounds.

Reduction of Sulphuric Acid.—If a strong (15 per cent.) solution of titanous sulphate is added slowly to concentrated sulphuric acid, reaction at once ensues; the amethyst colour of the titanous salt disappears and there is copious disengagement of sulphur dioxide. On adding larger amounts of the titanous sulphate solution, the reaction ceases owing to the dilution of the acid; sulphuric acid diluted with its own volume of water no longer reacts with titanous sulphate.

Quantitative Reduction of Nitric to Nitrous Acid.—The reduction of nitric acid to oxides of nitrogen and ammonia (*Ber.*, 1903, **36**, 166), to a stage intermediate between nitric oxide and nitrous oxide ("New Reduction Methods in Volumetric Analysis," p. 5), and quantitatively to ammonia (*J. Soc. Chem. Ind.*, 1915, **34**, 126) has been described.

Further experimental work on the subject, in which I have been ably assisted by Mr. J. H. Platt, has shown that if an acceptor, in the form of a primary aromatic amine, is present in the solution and the ratio $2TiCl_3 : HNO_3$ is adhered to, reduction of the nitric acid to nitrous acid is effected and a quantitative yield of the corresponding diazonium compound results, according to the general equation—

$$Ar{\cdot}NH_2,HCl + HNO_3 + 2TiCl_3 + 2HCl = Ar{\cdot}N{:}NCl + 2TiCl_4 + 3H_2O.$$

The nitrates of aniline, *o*- and *p*-toluidines, α-naphthylamine, benzidine, and dianisidine, when thus treated in dilute aqueous solution in presence of hydrochloric acid, gave the corresponding diazonium compounds in quantitative yields. The reaction takes place, under these conditions, rapidly at the ordinary temperature, and in dilute solution no appreciable rise in temperature is apparent.

So far, the reaction has not given good results with the nitrates of the nitro-amines; the nitro-group apparently reacts simultaneously with the reducing agent and this gives rise to complications. The diazotisation of aminoazobenzene by this reaction was likewise unsuccessful. Nitrosodimethylaniline was obtained in only 16 per cent. of the theoretical yield, and *p*-nitrosophenol in amount only sufficient for its identification. On the other hand, β-naphthol, treated with the theoretical amounts of nitric acid and titanous chloride, gave good yields of nitrosonaphthol.

The primary aromatic amines above referred to were diazotised by dissolving a known weight of the pure base in a sufficiency of dilute hydrochloric acid, making the solution approximately $N/10$ with cold water, and adding exactly one equivalent of $N/10$-nitric

acid followed, after stirring, by the theoretical amount of titanous chloride (2 equiv.), and stirring for about a minute (compare also Möhlau, D.R.-P. 25146, 1883; O. N. Witt, *Ber.*, 1909, **42**, 2953).

The titration of the resulting diazo-compounds was effected in the usual way, by running the diazo-solution into a freshly prepared standard solution of pure sodium β-naphthoxide in sodium carbonate. In one instance, the result of the ordinary titration was controlled by a titration with titanous chloride (reduction to the diazohydrazide) by Knecht and Thompson's method (*J. Soc. Dyers and Col.*, 1920, **36**, 215), rosinduline being employed as indicator.

In the results stated below, the amount of diazo-compound is given, for the sake of convenience, in terms of the primary amine.

Base.	Gram taken.	Gram found.	Base.	Gram taken.	Gram found.
Aniline	0·1261	0·1264	Benzidine	0·0920	0·0907
,, ...	0·3200	0·3187 (K. & T.)	Dianisidine	0·1322	0·1320
o-Toluidine	0·1548	0·1544	α-Naphthylamine	0·1350	0·1348
p-Toluidine	0·1436	0·1437			

Reduction of the Nitronaphthalenes.—In the titration of α-nitronaphthalene with titanous chloride, it was noticed that when hydrochloric acid was present in excess, the results were liable to come out too low, and it was consequently recommended (*op. cit.*, p. 130) that in carrying out this titration, no acid should be added, a sufficiency being present for the purpose in the standard titanous chloride solution. English (*J. Ind. Eng. Chem.*, 1920, **12**, 994), Callan, Henderson, and Strafford (*J. Soc. Chem. Ind.*, 1920, **39**, 86T), and Callan and Henderson (*ibid.*, 1922, **41**, 157T) have done further work on the titration of nitro-compounds with titanous chloride and Callan and Henderson have suggested the use of titanous sulphate in place of the chloride, all risk of the reaction taking an abnormal course being thereby avoided.

The immediate cause of the low results obtained in titrating with titanous chloride in presence of much hydrochloric acid appeared to be indicated in a paper by Seidler (*Ber.*, 1878, **11**, 1201), who obtained, besides α-naphthylamine, a considerable amount of a monochloronaphthylamine (m. p. 98°) on reducing α-nitronaphthalene with tin and concentrated hydrochloric acid. Although this observation made it probable that titanous chloride in presence of excess hydrochloric acid would effect a similar change, this had not been proved and the reaction has now been tried under various conditions of working and the products examined. It was found that when the amount of hydrochloric acid present was such as to satisfy the equation

$$C_{10}H_7{\cdot}NO_2 + 6TiCl_3 + 7HCl = C_{10}H_7{\cdot}NH_2{,}HCl + 2H_2O + 6TiCl_4,$$

the titration results were satisfactory. By increasing the acidity to 24HCl, it was found that, after reduction had gone to completion, a considerable amount of unchanged titanous chloride remained in the solution. On cooling, the latter deposited a considerable crop of crystalline plates with a metallic lustre, which were recrystallised twice from water to remove the titanium. The base isolated from these crystals was purified by recrystallisation from alcohol and from water and was ultimately obtained in long, hairy, almost colourless needles melting at 97° and having the composition $C_{10}H_6Cl{\cdot}NH_2$. Titrated with standard potassium bromate, it took up one equivalent of bromine, and it is evident from these data that it is 4-chloro-α-naphthylamine. From the yield obtained, this halogenated naphthylamine would appear to represent, under the conditions chosen, the main product of the reaction.

β-Nitronaphthalene, prepared by Sandmeyer's method (*Ber.*, 1887, **20**, 1407), was reduced under the same conditions, but no chlorination occurred, the resulting base consisting of pure β-naphthylamine. A normal result was also obtained in titrating this nitronaphthalene in presence of a large excess of hydrochloric acid. 1 : 8-Dinitronaphthalene also gave correct results when similarly titrated.

For the preparation of 4-chloro-α-naphthylamine, a solution of 10 grams of α-nitronaphthalene in 20 c.c. of hot alcohol was run slowly into a boiling solution of 278 c.c. of titanous chloride (20 per cent.) and 150 c.c. of concentrated hydrochloric acid, the boiling being continued for 6 minutes. The whole of the nitronaphthalene was reduced and the solution still contained a considerable amount of unchanged titanous chloride. The crystals of the hydrochloride that separated on cooling (11·6 grams), after recrystallising twice from water, were treated in aqueous solution with ammonia in slight excess. The separated base showed m. p. 93°, which is higher than the figure (85—86°) given by Atterberg (*Ber.*, 1887, **10**, 549) for 4-chloro-α-naphthylamine. After repeated recrystallisation from alcohol and from water, it was not found possible to raise the m. p. beyond 97°, whereas that stated by Reverdin (*Ber.*, 1900, **33**, 682) is 98° (Found: Cl = 20·11; *M*, by Rast's method, = 172·2. Calc. for $C_{10}H_8NCl$, Cl = 19·97 per cent.; *M* = 177·5).

The amount of bromine taken up by titration with potassium bromate was 0·0809 gram for 0·1696 gram of the base, which represents slightly more than one equivalent (0·0765 gram) per molecule.

4-Chloro-α-naphthylamine is readily diazotised and the diazo-compound combines completely with β-naphthol in alkaline solution, giving a scarlet, insoluble *azo*-compound, red needles, m. p.

213°, from alcohol (Found: Cl = 10·30. $C_{10}H_6Cl{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$ requires Cl = 10·67 per cent.). Sulphonated with fuming sulphuric acid, the product dyes wool a bright shade of scarlet.

In some further experiments on the effect of hydrochloric acid on the reduction of nitronaphthalene by titanous chloride, it was ascertained that with 12 mols. of hydrochloric acid a product resulted which showed m. p. between 80° and 90°. The highest yield of the monochloro-derivative appeared to be obtained by using 24 mols. of hydrochloric acid and an excess of 5 per cent. of titanous chloride over the 4 mols. required to produce the monochloro-compound. Under these conditions a 94 per cent. yield of crude 4-chloro-α-naphthylamine, m. p. 94°, was obtained.

Titrations.

(In collaboration with Miss E. HIBBERT.)

Tetramethyldiaminobenzhydrol, $OH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$ (Michler's hydrol).—This compound, although not used as a dyestuff, is of some importance as an intermediate product. Its solution in hydrochloric acid is colourless, but on the addition of excess of sodium tartrate, an intense blue colour at once develops. On titrating this solution with titanous chloride, the amount of the reagent required to decolorise is found to be exactly equivalent to two atoms of hydrogen. On exposing the reduced solution to the air, the blue colour returns immediately. This behaviour is not usual with the paraquinonoid compounds, and calls to mind that of many coloured compounds which are regarded as possessing an orthoquinonoid structure.

Of the phthaleins, only two have so far been titrated by means of titanous chloride, viz., eosin A and rhodamine B. It was considered of interest to add to these two further types and of these gallein and phenolphthalein were chosen. Both these compounds gave on titration the results which would have been expected by theory, *i.e.*, they each required amounts of titanous chloride for decoloration representing 2H. In the case of phenolphthalein, a simple means is thus afforded for the valuation of this drug, whilst in the case of gallein, the titration lends support to the quinonoid structure established by Orndorff and Brewer (*Amer. Chem. J.*, 1900, **23**, 425; 1901, **26**, 97).

Alizarin S.—It has been shown by Bradshaw and A. G. Perkin (J., 1922, **121**, 911) that β-hydroxyanthraquinone behaves abnormally on reduction, whereas anthraquinone itself gave a quantitative yield of anthranol under the same conditions. In these circumstances, it was thought that alizarin S might possibly not behave

towards reducing agents in the same way as alizarin, and the titration of this dyestuff was therefore tried. The sodium salt was titrated in presence of sodium tartrate in the same manner as is described for alizarin, flavo- and anthra-purpurin (*J. Soc. Dyers and Col.*, 1915, **34**, 241), and it was found that the solution gave the characteristic intense bluish-green colour * with the first drop of titanous chloride in excess of what would correspond to 4H. Its behaviour on reduction is therefore normal.

Tartrazine.—This dyestuff was prepared in the form of its pure crystallised tripotassium salt. For reduction with titanous chloride in presence of sodium tartrate to the disappearance of the yellow colour, it required the equivalent of 4H.

Isatin.—It is known that an aqueous solution of isatin is readily decolorised by acid reducing agents (Bayer, *Ber.*, 1879, **12**, 1309). The solution, on exposure to air, becomes yellow again, owing to regeneration of the isatin. Using titanous chloride as the reducing agent, it was found that the disappearance of the yellow colour coincided with the formation of dioxindole, according to the equation $C_8H_5O_2N + H_2 = C_8H_7O_2N$. By employing a trace of patent-blue as indicator, the end-point (yellow-green-blue-colourless) is rendered more distinct, especially in artificial light. Rhodamine B also may serve as indicator, but all the other dyestuffs tried for the purpose were reduced before the isatin was affected.

Phenylhydrazine.—Although phenylhydrazine is not acted upon by titanous chloride, it can nevertheless be accurately titrated by means of this reagent using an indirect method. It has been found, namely, that 1 mol. of methylene-blue requires for its reduction to the leuco-compound exactly 1 mol. of phenylhydrazine. The end-point obtained in the direct titration is not sufficiently sharp to ensure that degree of accuracy which is required in volumetric analysis. By adding the phenylhydrazine to an excess of methylene-blue, boiling for about a minute in a current of carbon dioxide, and titrating back the excess with titanous chloride, accurate results have been obtained. Nitrogen is evolved during the reduction (see also Landauer, Inaug. Dissert., Munich, 1909), which evidently takes place in the following sense:

$$C_{16}H_{18}N_3ClS + C_6H_8N_2 = C_6H_6 + C_{16}H_{20}N_3ClS + N_2.$$

Glucosazone.—E. Fischer (*Ber.*, 1886, **19**, 1920) has expressed

* Besides being shown by the compounds named, this colour is shown by the α-amino- and hydroxy-anthraquinones, quinizarin, anthrarufin, α-aminoalizarin (alizarin claret), and purpurin, but not by anthraquinone, the β-amino- and hydroxy-anthraquinones, β-nitroalizarin, nor by anthragallol. The colour is instantly destroyed by the addition of a ferric salt.

the view that the reduction of this compound by zinc and acetic acid takes place according to the equation

$$C_{18}H_{22}O_4N_4 + 6H + H_2O = C_6H_{13}O_5N + NH_3 + 2C_6H_5{\cdot}NH_2.$$

It is now found that in carrying out the titration with titanous chloride in presence of sodium tartrate, the amount of hydrogen required is exactly that shown in the above equation. In order to obtain a suitable end-point, it was found convenient to effect the reduction with excess of titanous chloride and to titrate the excess with crystal-scarlet or lanacyl-blue. The reaction has been successfully applied to the quantitative estimation of glucose. It is hoped to give details of the method in a further communication.

Details of Analytical Methods.

Tetramethyldiaminobenzhydrol.—The hydrol (purified by crystallisation from tetralene; m. p. 98°) was dissolved in dilute hydrochloric acid, excess of sodium tartrate added, and titration effected in an atmosphere of carbon dioxide to the disappearance of the blue colour. 0·1042 Gram of substance required 22·0 c.c. of $TiCl_3$ (1 c.c. = 0·001958 gram of Fe), and as 270 grams of the hydrol = 112 grams of iron, the amount present was 99·7 per cent.

Phenolphthalein.—An alcoholic solution is run into water, about 2 c.c. of a saturated solution of sodium tartrate are added, and the titration is then proceeded with as in the case of gallein. The end-point is ascertained by allowing a drop to coalesce on a spot-plate with a drop of caustic soda solution, when it will have ceased to give the characteristic red colour. 0·1005 Gram of phenolphthalein (m. p. 256°) required 20·2 c.c. of $TiCl_3$ (1 c.c. = 0·001755 gram of Fe) and on the basis of 1 mol. of phenolphthalein requiring 2H for its reduction to phenolphthalein this gives 100·1 per cent. Another estimation gave 99·9 per cent.

Gallein.—Since this compound does not show any definite m. p. and it was necessary, in order to verify the accuracy of the method, to have a guarantee of its purity, the tetra-acetyl compound was prepared in the crystallised state from commercial gallein. This showed m. p. 242°, which is in accordance with the figure found by Orndorff and Brewer (*loc. cit.*). From the acetyl compound, the gallein was obtained in a crystallised state by hydrolysing with a small amount of concentrated sulphuric acid, diluting with water, and allowing to stand over-night. The characteristic, well-defined crystals of gallein thus obtained were washed with water and dried. In carrying out the titration, an alcoholic solution of a known weight of gallein was run into 2 c.c. of a saturated solution of sodium tartrate and about 20 c.c. of water, the solution was then

warmed at about 50° and titrated with standard titanous chloride, in a current of carbon dioxide, until the magenta colour gave place to a pale yellow. 0·1001 Gram of gallein required 28·7 c.c. of $TiCl_3$ (1 c.c. = 0·001019 gram of Fe) and assuming that 2H have been required for the reduction, this gives gallein 94·93 per cent.; water at 110° 4·77 per cent. (calc. for 1 mol., 4·71): total 99·70 per cent.

Alizarin S.—The titration is effected by adding excess of titanous chloride to a solution of a known weight of the dyestuff in water containing excess of sodium tartrate. The solution is boiled in a current of carbon dioxide, and a measured volume of titanous chloride run in. The excess of the latter is ascertained by back-titration with iron alum to the disappearance of the blue-green coloration. 0·0511 Gram of alizarin S required 15·0 c.c. of $TiCl_3$ (1 c.c. = 0·002112 gram of Fe): colouring matter = 94·6; water at 110° = 5·11 (calc. for 1 mol., 5·0): total = 99·71 per cent.

Sodium as sulphate, in the anhydrous substance = 20·64 (required by theory, 20·76 per cent.).

Tartrazine.—This substance is titrated direct in hydrochloric acid solution and at an elevated temperature, like an ordinary mono-azo-dye. The disappearance of the yellow colour is taken as the end-point. 0·1931 Gram of substance required 23·1 c.c. of $TiCl_3$ (1 c.c. = 0·002771 gram of Fe) and assuming that 582 parts of the dye require 224 of iron, the following result is obtained: tartrazine = 86·11; water at 110° = 13·98 (calc. for $5H_2O$, 13·93): total 100·00 per cent.

The purity of the dyestuff was controlled by an estimation of the potassium (Found: K = 44·67. Calc. for $C_{16}H_9O_9N_4S_2K_3$, K = 44·84 per cent.).

Isatin.—The isatin was crystallised from water and had m. p. 201°. The titration offers no difficulty, reduction to the colourless dioxindole taking place at the ordinary temperature in a current of carbon dioxide and without any additions. 0·04347 Gram of substance in 50 c.c. of water required 36·3 c.c. of $TiCl_3$ (1 c.c. = 0·001016 gram of Fe), denoting 99·82 per cent. purity.

With patent-blue as indicator, the same sample gave 99·8 per cent. Although of no value as a dyestuff, isatin is employed in considerable amounts in the manufacture of certain indigoid vat dyes.

Estimation of Phenylhydrazine.—Phenylhydrazine (0·3320 gram) was dissolved in hydrochloric acid and made up to 100 c.c. and to 10 c.c. of the solution 50 c.c. of methylene-blue (1 c.c. = 0·001244 gram of Fe) were added. The solution was boiled in a current of carbon dioxide, and the excess of methylene-blue titrated with

titanous chloride (1 c.c. = 0·001275 gram of Fe) of which 26·7 c.c. were required. Since 108 of phenylhydrazine = 122 of Fe, the amount present was 98·8 per cent. An estimation carried out in a similar way on a phenylhydrazine from a different source gave 99·3 per cent., whilst Kahlbaum's product taken fresh from a sealed vessel gave 99·8 per cent.

In consequence of the facility with which phenylhydrazine can be estimated by the above method, an attempt was made to determine the phenylhydrazine in the products of acid hydrolysis of a known weight of glucosazone. To this end, 0·322 gram of glucosazone was warmed with concentrated hydrochloric acid and the resulting product made up to 100 c.c. To 10 c.c. of this solution, 50 c.c. of methylene-blue (1 c.c. = 0·001244 gram of Fe) were added, the mixture was heated to boiling in a current of carbon dioxide, and the excess of methylene-blue titrated back with titanous chloride (1 c.c. of $TiCl_3$ = 0·001275 gram of Fe), of which 15·7 c.c. were required. Since 216 of phenylhydrazine are formed from 358 of glucosazone, the result, expressed in terms of the latter, represents 99·75 per cent.

Reduction of Phenylglucosazone.—To a solution of 0·02915 gram of glucosazone in alcohol, 2 c.c. of a saturated solution of sodium tartrate were added and 50 c.c. of titanous chloride were run in. After the mixture had boiled in an atmosphere of carbon dioxide for 6 minutes, excess of hydrochloric acid was added and the excess of titanous chloride titrated back with crystal-scarlet. This showed 34·2 c.c. excess $TiCl_3$. 15·8 C.c. of $TiCl_3$ (1 c.c. = 0·001736 gram of Fe) had therefore been consumed in the reduction, and assuming 358 of glucosazone to be equivalent to 336 of Fe (6H), this gives 99·85 per cent. 0·0694 Gram of glucosazone, treated as above with 50 c.c. $TiCl_3$ (1 c.c. = 0·001712 gram of Fe) and the excess afterwards estimated with crystal-scarlet, showed 12·1 c.c. excess; that is, 37·9 c.c. were used by the glucosazone, which is equivalent to 99·6 per cent.

In another experiment, 0·02550 gram of glucosazone, reduced in the same way and back-titrated with lanacyl-blue, used up 8·6 c.c. of $TiCl_3$ (1 c.c. = 0·002771 gram of Fe), which represents 0·02538 gram, or 99·5 per cent. of glucosazone.

Summary.

It is shown that, under chosen conditions, titanous chloride reduces nitric acid quantitatively to nitrous acid. The reaction may be employed as a convenient means for diazotising primary aromatic amines.

By reducing α-nitronaphthalene with titanous chloride in pres-

ence of a large excess of hydrochloric acid, the principal product of the reaction (about 94 per cent.) is 4-chloro-α-naphthylamine.

Methods are described for the volumetric estimation of tetramethyldiaminobenzhydrol, phenolphthalein, gallein, alizarin S, tartrazine, isatin, glucosazone, and phenylhydrazine. The last-named substance may also be accurately estimated in the products of the acid hydrolysis of glucosazone.

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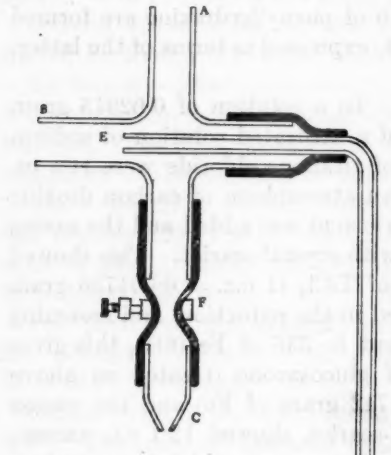
[*Received, April 9th,* 1924.]

NOTES.

Device for Maintaining a Constant Level in a Water-bath. By RICHARD BROOKS.



THE figure shows a device for maintaining a constant level in a boiling-water bath. Water, which may be taken direct from the outflow of a reflux condenser if this is being used, enters at *A*, and the stream divides between *B* and *C*. Air is drawn through *DE* by the stream of water and by the hydrostatic tension of the column of water between *B* and the outlet in the sink. When the water level reaches *D*, water is withdrawn from the bath through *DE*. The screw-clip, *F*, controls the rate of flow of water into the bath, and is adjusted until the water level is just maintained at *D*. — EXETER COLLEGE, OXFORD.

[*Received, May* 21*st,* 1924.]

A Simple Non-splash Ring for Use with Scheibler's Desiccator. By S. C. BRADFORD.

THE possible contamination of material by splashes from sulphuric acid in a Scheibler's desiccator can be avoided effectively by allowing a glass bell-shaped ring to rest with the narrower end downwards on the constriction of the acid reservoir. The ring projects

about 2 centimetres into the reservoir. The rings to fit desiccators of the ordinary sizes can be bought from Messrs. Gallenkamp.—THE SCIENCE MUSEUM, S.W. 7. [*Received, April 4th*, 1924.]

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*4-Nitro-2-sulphophenyldehydrothio-*p*-toluidinesulphonic Acid.* By DAVID HENRY PEACOCK.

A MIXTURE of 34 grams of sodium dehydrothio-*p*-toluidinesulphonate, 29 grams of sodium 6-chloro-3-nitrobenzenesulphonate, 11 grams of calcium carbonate, and 180 c.c. of water is boiled under reflux for several days or, better, heated at 120° in an autoclave. The reaction is slow; after 48 hours' boiling under reflux, more than 60 per cent. of the dehydrothiotoluidinesulphonate is unchanged. The crude sulphonic acid precipitated from the filtered, boiling, acidified solution is stirred with hot water and excess of ammonia; on cooling, most of the ammonium dehydrothiotoluidinesulphonate crystallises. The sulphonic acid reprecipitated from the filtrate is converted into the *potassium* salt, which, crystallised from water and from aqueous alcohol, forms small, orange crystals (Found: K = 12·3. $C_{20}H_{13}O_8N_3S_3K_2$ requires K = 13·0 per cent.). This product dyes cotton in bright yellow shades slightly tinged with green.

The *silver*, *lead*, and *barium* salts have been prepared. Strong caustic potash solution and the potassium salt react, best in alcoholic solution, to give a bronzy, crystalline powder, which regenerates the potassium salt on treatment with water and appears to contain the :NK group.

*4-Amino-2-sulphophenyldehydrothio-*p*-toluidinesulphonic acid*, prepared by reducing the nitro-salt with iron and acetic acid, is a pale yellow, almost white, crystalline powder (Found: K = 13·5. $C_{20}H_{15}O_6N_3S_3K_2$ requires K = 13·7 per cent.) which dyes cotton in extremely pale shades. The diazo-compound, which appears to be very stable, couples on the fibre, producing with β-naphthol a bright rose, and with *m*-phenylenediamine a full brown shade.

I wish to thank the British Dyestuffs Corporation for most of the materials used in this work and for permission to publish the results.—UNIVERSITY COLLEGE, UNIVERSITY OF RANGOON, BURMA. [*Received, January 21st*, 1924.]

CCI.—*Colour and Molecular Geometry. Part II. Explanation of the Results of Chattaway and Clemo.*

By JAMES MOIR.

CHATTAWAY and CLEMO have recently published the results of a most painstaking investigation into the reason why substances of the types $NO_2 \cdot C_6H_4 \cdot NH \cdot N{:}CHPh$ and $NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot NHPh$ give deep colours (violet to green) when dissolved in alcoholic caustic alkali, although the substances themselves have only the "low" colours of the nitroaniline class (J., 1923, **123**, 3041). This phenomenon is obviously analogous to the behaviour of *p*-nitrobenzeneazo-α-naphthol, which changes from orange to blue when treated with alkali (Hewitt, J., 1907, **91**, 1251). Chattaway and Clemo adopt the principles of Hewitt's theory to explain the "high" colours given by their substances, these principles being mainly that a long chain of alternate double and single bonds connotes a "high" colour, and that quinonoid benzene rings are to be included in the chain.

Considering the para-isomerides only, the formulæ are :—

(1) $KO_2N{:}C_6H_4{:}N \cdot N{:}CHPh$ (violet)
(2) $KO_2N{:}C_6H_4{:}CH \cdot N{:}NPh$ (green)
(3) $KO_2N{:}C_6H_4{:}N \cdot N{:}C_{10}H_6{:}O$ (blue)

The author has examined spectroscopically such of Chattaway and Clemo's substances as are necessary for obtaining numerical data to compare with the absorption of less complicated substances, and has also observed the absorption of such of the simpler substances as have not already been the subject of publication as regards the position of their absorption band.

Table I exhibits the observations made in presence of alcoholic potash, the substances being arranged in order of "height" of colour, beginning with green and passing through blue, violet, rose, salmon, and orange to yellow, as the complexity of the substances diminishes. It is to be noted that the nitrohydrazones are not good subjects for spectroscopy, since their bands, at the best concentration of the solutions, are exceedingly wide as compared with those of the majority of coloured substances. Thus 600 in the table means a band well-defined between 560 and 640 but fading indefinitely through 15 units at the edges, and with the centre in doubt by about 10 units ($\mu\mu$). Such bands are best observed with a small, direct-vision instrument and an intense source of light.

The table includes, in addition to the nitrohydrazones and the simple substances, certain derivatives of diazoaminobenzene and of

benzylidenebenzylamine. These are related to Chattaway and Clemo's substances by the substitution of ·N: for ·CH:, and of ·CH_2· for ·NH·, respectively.

TABLE I.

Table showing the depression of colour as the nitrohydrazones are degraded towards the parent-substances.

Note.—All observations were made with alcoholic potash solutions.

Centre of absorption band.	Name of substance.	Nature of degradation.
700	(1) *p*-Nitrobenzaldehyde-phenylhydrazone.	
600	(2) *p*-Nitrobenzaldehyde-*p*-nitrophenylhydrazone.	Orbit from end to near the middle only: partial suppression of $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH$ orbit.
545	(3) Benzaldehyde-*p*-nitrophenylhydrazone. (4) Benzophenone-*p*-nitrophenylhydrazone.	Total suppression of CH part of orbit: orbit is $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N$.
	(5) *pp'*-Dinitrodiazoaminobenzene.	Substitution of N for CH in substance (2).
510	(6) *p*-Nitrodiazoaminobenzene.	Substitution of N for CH in (3).
490	(7) Benzylidene-*p*-nitrobenzylamine. (8) *p*-Nitrophenylacetonitrile.	Substitution of CH_2 for NH in (1) or (3). (?) Formation of $NO_2K{:}C_6H_4{:}C{:}C{:}NK$.*
470	(9) *p*-Nitrobenzaldehyde-phenylbenzylhydrazone. (10) *p*-Nitrobenzylidene-*p*-nitrobenzylamine.	One end of (1) rendered inactive. Orbit of (7), but to near the middle only.
460 †	(11) *p*-Nitrophenylhydrazine.	Parent-substance of (2), (3), (4), etc.
450	(12) *p*-Nitrodibenzylamine.	(7) plus two hydrogen atoms.
430	(13) Benzyl-*p*-nitroaniline. (14) *p*-Nitrobenzylamine.	Isomerides, being (12) less a benzyl group.
415	(15) Benzylidene-*p*-nitroaniline. (16) *p*-Nitroaniline. (17) *p*-Nitrosophenol.	More primitive parent-substances. They have also a lower band at 250.
395	(18) *p*-Nitrophenol.	
352	(19) *p*-Nitrobenzaldehyde.	Probably does not react with KOH.

* Compare $O{:}C_6H_4{:}N{\cdot}N{:}NK$ (J., 1907, **91**, 1255).

† Nitrodeoxybenzoin and nitrobenzylaniline also have this colour.

The author is of the opinion that the orbit theory gives a better account of the phenomena embodied in the table than the Hewitt theory. It is notorious that alternate double and single linkings *per se* do not necessarily lead to high colour (for example, hexatriene and cinnamaldehyde).

As a detailed explanation the author suggests that in substance No. 1, with the highest colour, the orbit of an electron grazes the outside of the chain $O_2N{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N$. When CH_2 is substituted for NH at the end of this chain (substance 7), the possibility of ionisation of the end group is removed,* and the orbit goes round $O_2N{\cdot}C_6H_4{\cdot}CH{:}N$, in agreement with the much lower colour observed.

It is to be noted that the formulæ $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}CH_2Ph$ and $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{:}CHPh$ are to be considered as tautomeric, just as in the case of nitrodiazoaminobenzene, which is either $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}NPh$ or $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NHPh$.

It would be interesting to observe the colour of the substance $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CHPh$ to see whether the further replacement of N by CH would render the substance almost colourless in alcoholic potash.

The orbit of *p*-nitrophenylhydrazine in alcoholic potash may be supposed to cover the whole molecule, namely, $NO_2{\cdot}C_6H_4{\cdot}N{\cdot}N$, giving a colour not very different from that due to the orbit $NO_2{\cdot}C_6H_4{\cdot}CH{:}N$ just supposed for benzylidenenitrobenzylamine. In substance (3) the extra benzylidene group, although not ionisable, constitutes a heavy "loading" on the nitrophenylhydrazine orbit, and changes the colour from orange to violet. It is suggested that the distance between the foci of the orbit in substance 3 is the same as in substance 11, but that as the electron has to go round the benzylidene group, the ellipse is much rounder (with a lower eccentricity); whereby, from Roseveare's equation (see Part I, this vol., p. 1134), the absorption band is much raised in position.

Too little is known about the angles which the carbon and nitrogen atoms in such chains make with one another, to enable the geometry of the system to be attacked in detail, but the difference between the isomeric substances (1) and (3) may (in addition to the explanation given above) partly depend on the fact that the angle of the junction N·NR is much more obtuse than the tetrahedral angle of carbon junctions.

It is to be noted that on the new theory the heightening of colour by "loading" consists in the existence of a wider orbit (with a lower eccentricity for the same interfocal distance) due to the moving electron having to go round an obstacle.

The fact that benzophenone-*p*-nitrophenylhydrazone has much the same colour in potash solution as the benzaldehyde compound shows, as Chattaway and Clemo point out, that a hydrogen atom at the end of this chain is not necessary for the production of the high colour. The fact also supports the orbit theory, inasmuch as

*–NK can be formed, but not –CHK.

this particular hydrogen atom belongs to the " load " and is outside the positive centres on which the colour really depends, that is, outside the group $O_2N{\cdot}C_6H_4{\cdot}NH{\cdot}N$. Similarly, the low colour of substance (9) belongs to the orbit $O_2N{\cdot}C_6H_4{\cdot}CH{:}N$, and is that of a loaded *p*-nitrobenzylamine, similar to that of substance (7) already discussed.

It is probable that the remaining member of the series, isomeric with No. (9) but not observed either by Chattaway and Clemo or by myself, namely, $NO_2{\cdot}C_6H_4{\cdot}N(C_7H_7){\cdot}N{:}CHPh$, will also prove to have a low colour in alcoholic potash solution.

It will probably be of interest to append a table of observations of the positions of the band of some of these substances in the absence of potash, and, in addition, of the fundamental substances of the aromatic series. In many cases isomeric substances of widely different character have their band in the same place, for example, *p*-nitroaniline and *p*-benzoquinonedioxime.

TABLE II.

Free substances (in absence of KOH).

Centre of absorption band.	Name of substance.
395	(1) *p*-Nitrophenylhydrazine.
	(2) Benzyl-*p*-nitroaniline.
370	(3) *p*-Nitroaniline (also quinonedioxime).
360	(4) *p*-Nitrobenzylideneaniline.
	(5) Benzylidene-*p*-nitroaniline.
340	(6) *p*-Nitrostilbene.
325	(7) *p*-Nitrobenzylamine.
315	(8) Benzylideneaniline.
310	(9) Nitrosophenol.
	(10) Nitrophenol.
293	(11) Stilbene.
285	(12) Benzaldehyde (also aniline).
275	(13) Phenol.
265	(14) Nitrobenzene (vague).
255	(15) Benzene (average of several observations).

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ADDENDUM.—The remarkable bathychromic effect of replacing the group NHPh in this series by hydroxyl should be mentioned. Thus *p*-nitrobenzaldoxime, which is substance 1 with OH for NHPh, is only orange in alcoholic potash (λ 450); and potassium *p*-nitrobenzenediazotate, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}OK$, which is substance 6 with the same substitution, is colourless (Hantzsch gives λ 326). This lowering of colour is probably of steric origin, the oxygen being brought near the nitro-group.

CCII.—*Halogen-substituted Aryl Thiocarbimides.*

By Frederick Daniel Chattaway, Richard Kenneth Hardy, and Hedley George Watts.

Although Hofmann's method (*Annalen*, 1846, **57**, 256) of preparing the thiocarbimides (mustard oils), involving the intermediate formation of a thiocarbamide, has hitherto been regarded as quite general, the reactions involved are profoundly influenced by the nature of a nuclear substituent in the primary aromatic amine.

The readiness with which both reactions take place appears to depend largely on the basicity of the amine employed. Aniline and *o*- and *p*-toluidine react readily with carbon disulphide, whilst their monohalogen-substituted derivatives react with difficulty, and the dihalogen-substituted derivatives scarcely, if at all. It therefore appeared probable that if a mixed thiocarbamide could be obtained in which one of the substituting groups was derived from a halogen-substituted amine and the other from a more basic amine it would be possible to remove the latter by an acid, leaving the less positive group in the resulting mustard oil.

Such mixed thiocarbamides can be obtained by the interaction of phenylthiocarbimide, which is easily made, with various halogen-substituted anilines and it has been found that these decompose in the expected manner, giving a new and simple method of preparing the hitherto little-studied halogen-substituted mustard oils, *e.g.*, 2 : 4-dichlorophenylthiocarbimide:

$$C_6H_3Cl_2\cdot NH_2 \xrightarrow{PhNCS} C_6H_3Cl_2\cdot NH\cdot CS\cdot NHPh \xrightarrow{H_2SO_4aq.} C_6H_3Cl_2\cdot NCS + NH_2Ph,H_2SO_4.$$

By this method, the monohalogen- and the hitherto undescribed 2 : 4-dihalogen-substituted aryl mustard oils have been obtained, the yield in all cases being very satisfactory.

Experimental.

The halogen-substituted thiocarbimides are best prepared by heating the substituted amines with the equivalent amounts of phenylthiocarbimide and decomposing the resulting *as*-halogen-substituted thiocarbamide by heating with dilute sulphuric acid of a suitable strength in a current of superheated steam, this yielding the halogen-substituted thiocarbimide mixed with a certain amount of re-formed phenylthiocarbimide. These can, however, easily be separated by fractional distillation in steam, the unsubstituted thiocarbimide distilling over more readily than the substituted.

The aniline and the small quantity of substituted aniline produced remain behind in combination with the sulphuric acid. The substituted base can be recovered and used again.

The halogen-substituted mustard oils react as readily as the unsubstituted, yielding mixed carbamides with ammonia and amines and substituted urethanes with alcohols.

p-*Chlorophenylthiocarbimide*, $C_6H_4Cl{\cdot}NCS$.—A mixture of 12·5 grams of *p*-chloroaniline (1 mol.) and 13·5 grams of phenylthiocarbimide (1 mol.) was heated on a water-bath for 2 to 3 hours until it solidified, 150 grams of sulphuric acid diluted with 100 grams of water were added, and the mixture was distilled in a current of superheated steam, the level of the liquid in the flask being kept constant by regulating the superheating of the steam. The oily mixture of phenyl- and *p*-chlorophenyl-thiocarbimides in the distillate partly solidified.

The two compounds were separated by a fractional distillation in steam, the distillate being collected in 14 fractions. On standing for some hours at the ordinary temperature, the oily drops separating from the fractions 9—14 solidified partly or wholly to soft, white, crystalline masses. These were removed and the still unsolidified part was separated by filtration under pressure. The liquid portion was mixed with the liquids separating from fractions 6—8 and again fractionally distilled in steam, 14 fractions being collected; solid material was obtained as before from fractions 11—14. The process was repeated until no more solid separated. The whole mixed solid product thus obtained melted at 41°.

By a further fractional distillation in steam, pure *p*-chlorophenylthiocarbimide was isolated (yield about 30 per cent. of the theoretical, calculated from the amount of *p*-chloroaniline used) as a mass of colourless, interlacing crystals, m. p. 44·5°. The compound is difficult to crystallise from any solvent on account of its low melting point.

p-*Chlorophenylthiocarbamide*, $C_6H_4Cl{\cdot}NH{\cdot}CS{\cdot}NH_2$, is formed when *p*-chlorophenylthiocarbimide is warmed with concentrated aqueous ammonia. It is moderately easily soluble in boiling alcohol, from which it separates in colourless needles, m. p. 178°.

o- and *m*-Chlorophenylthiocarbimides can be similarly prepared, as can also the corresponding bromo-derivatives.

2 : 4-*Dichlorophenylthiocarbimide*, $C_6H_3Cl_2{\cdot}NCS$.—2 : 4-Dichlorodiphenylthiocarbamide was prepared quantitatively by heating together equivalent amounts of phenylthiocarbimide and 2 : 4-dichloroaniline at 100° for 2 hours. The thiocarbamide is not produced if the mixture is too strongly heated: for example, heating the two compounds together over a flame to boiling

causes profound decomposition and formation of much tarry matter.

To prepare the thiocarbimide, 100 grams of the crude powdered 2 : 4-dichlorodiphenylthiocarbamide were mixed with 200 grams of water and 300 grams of sulphuric acid and distilled with superheated steam as before, a mixture of phenylthiocarbimide with a much larger quantity of 2 : 4-dichlorophenylthiocarbimide separating from the distillate as oily drops which partly solidified on standing. The semi-solid, oily product was separated and again fractionally distilled in superheated steam, the distillate being collected in 25 fractions. The liquid separating from fractions 1—4 did not solidify on cooling, that from the remaining fractions did. This solid was separated, strongly pressed between filter-paper, and again fractionally distilled with superheated steam. A very little oily product which would not solidify on standing separated as before from the first fraction, that from the remaining fractions was filtered off at a pump, dried in a desiccator, and distilled; b. p. 208°/17·5 mm. It was finally purified by crystallisation from chloroform, in which it was readily soluble and from which it separated in clusters of colourless, irregular plates, m. p. 39°. It has a slight odour recalling that of phenylthiocarbimide (Found: Cl = 34·66. $C_7H_3NCl_2S$ requires Cl = 34·76 per cent.).

2 : 4-*Dichlorophenylthiocarbamide*, $C_6H_3Cl_2{\cdot}NH{\cdot}CS{\cdot}NH_2$, is formed when excess of strong aqueous ammonia is added to alcoholic 2 : 4-dichlorophenylthiocarbimide. It is slightly soluble in water, but readily soluble in alcohol, from which it separates in colourless, glistening plates, m. p. 158° (Found: Cl = 32·37. $C_7H_6N_2Cl_2S$ requires Cl = 32·08 per cent.).

When it is heated with alcohols for several hours, 2 : 4-dichlorophenylthiocarbimide forms the corresponding 2 : 4-dichlorophenylthiocarbamates. The *methyl* ester, $C_6H_3Cl_2{\cdot}NH{\cdot}CS{\cdot}OMe$, colourless plates, m. p. 48·5°, from chloroform (Found: Cl = 29·57. $C_8H_7ONCl_2S$ requires Cl = 30·04 per cent.), *ethyl* ester, colourless plates, m. p. 79°, from alcohol (Found: Cl = 28·0. $C_9H_9ONCl_2S$ requires Cl = 28·36 per cent.), and the n-*propyl* ester, colourless needles, m. p. 72°, from chloroform (Found: Cl = 27·16. $C_{10}H_{11}ONCl_2S$ requires Cl = 26·85 per cent.), were prepared.

2 : 4-*Dibromophenylthiocarbimide*, prepared and isolated in a similar manner to the corresponding 2 : 4-dichloro-compound, is readily soluble in warm chloroform, from which it separates in very pale yellow, compact rhombs, m. p. 59·5°. It has a slight odour similar to that of the corresponding dichloro-compound and gives all the characteristic reactions of an aryl thiocarbimide (Found: Br = 54·9. $C_7H_3NBr_2S$ requires Br = 54·56 per cent.).

2 : 4-*Dibromophenylthiocarbamide*, $NH_2 \cdot CS \cdot NH \cdot C_6H_3Br_2$, prepared from excess of strong aqueous ammonia and hot alcoholic 2 : 4-dibromophenylthiocarbimide, is readily soluble in alcohol, from which it separates in colourless plates, m. p. 170° (Found : Br = 51·9. $C_7H_6N_2Br_2S$ requires Br = 51·58 per cent.).

Ethyl 2 : 4-*dibromophenylthiocarbamate*, m. p. 62° (Found : Br = 47·54. $C_9H_9ONBr_2S$ requires Br = 47·15 per cent.), and the corresponding n-*propyl* ester, m. p. 68° (Found : Br = 45·45. $C_{10}H_{11}ONBr_2S$ requires Br = 45·28 per cent.), separate from alcohol and chloroform, respectively, in colourless, rhombic prisms.

During the course of this investigation several *n*-butyl urethanes have been prepared and their properties are here recorded.

n-*Butyl phenylthiocarbamate*, m. p. 55° (Found : N = 6·72. $C_{11}H_{15}ONS$ requires N = 6·70 per cent.), and n-*butyl* p-*tolylthiocarbamate*, m. p. 65° (Found : N = 6·31. $C_{12}H_{17}ONS$ requires N = 6·27 per cent.), separate from alcohol in colourless needles.

For purposes of comparison, a number of unsymmetrical halogen-substituted thiocarbamides have been made by heating various arylthiocarbimides with various halogen-substituted anilines.

p-*Chlorophenyl*-p-*tolylthiocarbamide*, $C_6H_4Cl \cdot NH \cdot CS \cdot NH \cdot C_7H_7$, colourless plates, m. p. 173°, from boiling acetic acid (Found : N = 9·85. $C_{14}H_{13}N_2ClS$ requires N = 10·13 per cent.).

p-*Chlorophenyl*-o-*tolylthiocarbamide*, colourless, needle-shaped crystals, m. p. 119·5°, from boiling alcohol (Found : N = 9·89 per cent.).

p-*Bromophenyl*-p-*tolylthiocarbamide*, needles, m. p. 182°, from boiling acetic acid (Found : N = 8·47. $C_{14}H_{13}N_2BrS$ requires N = 8·72 per cent.).

2 : 4-*Dichlorodiphenylthiocarbamide*, needles, m. p. 157°, from boiling alcohol (Found : N = 9·37. $C_{13}H_{10}N_2Cl_2S$ requires N = 9·43 per cent.).

2 : 4-*Dibromodiphenylthiocarbamide*, needles, m. p. 165°, from boiling alcohol (Found : N = 7·53. $C_{13}H_{10}N_2Br_2S$ requires N = 7·26 per cent.).

2 : 4-*Dichlorophenyl*-p-*tolylthiocarbamide*, needles, m. p. 145°, from boiling alcohol (Found : N = 8·70. $C_{14}H_{12}N_2Cl_2S$ requires N = 9·01 per cent.).

THE QUEEN'S COLLEGE, OXFORD. [*Received, March 26th*, 1924.]

CCIII.—*Application of the Grignard Reaction to some Acetylenic Compounds. Part II.*

By FORSYTH JAMES WILSON and WILLIAM MCNINCH HYSLOP.

As circumstances have arisen which preclude a continuation of the work described in Part I (J., 1923, **123**, 2612), it has been decided to communicate the results obtained so far.

$\alpha\theta$-Diphenyl-$\gamma\zeta$-dimethyl-$\Delta^{\alpha\eta}$-octadi-inene-$\gamma\zeta$-diol (α-modification), on heating with sulphuric acid, was converted into 2 : 5-*diphenylacetylenyl*-2 : 5-*dimethyltetrahydrofuran*,

$$\begin{matrix}CH_2\cdot CMe(OH)\cdot C{:}CPh \\ | \\ CH_2\cdot CMe(OH)\cdot C{:}CPh\end{matrix} = \begin{matrix}CH_2\cdot CMe\cdot C{:}CPh \\ | \quad >O \\ CH_2\cdot CMe\cdot C{:}CPh\end{matrix} + H_2O,$$

behaving in this respect like other 1 : 4-glycols. Except for some charring, $\alpha\zeta$-diphenyl-$\gamma\delta$-dimethyl-$\Delta^{\alpha\epsilon}$-hexadi-inene-$\gamma\delta$-diol was unaffected by this treatment. Both glycols were attacked by boiling sodium hydroxide solution, phenylacetylene and an unworkable tarry product being formed in each case.

Attempts were made to obtain acetylenic ketols. Diacetyl and magnesium phenylacetylenyl bromide, in equimolecular proportion, gave the ketol *α-phenyl-γ-methyl-Δ^{α}-pentinene-γ-ol-δ-one*, $COMe\cdot COMe + CPh{:}C\cdot MgBr \longrightarrow COMe\cdot CMe(OH)\cdot C{:}CPh$, together with the glycol previously described. Acetonylacetone when subjected to this reaction failed to give a ketol, the glycol only being obtained. In similar cases, the monomethylphenylhydrazone of a diketone has been successfully employed by Diels and Kollisch (*Ber.*, 1911, **44**, 264), but in this particular instance no reaction took place.

Two tetra-acetylenic glycols have been prepared. Ethyl oxalate and magnesium phenylacetylenyl bromide gave *$\alpha\alpha\beta\beta$-tetraphenylacetylenylethylene glycol*,

$$CO_2Et\cdot CO_2Et + 4CPh{:}C\cdot MgBr \longrightarrow HO\cdot C(C{:}CPh)_2\cdot C(C{:}CPh)_2\cdot OH;$$

in a similar manner ethyl succinate yielded *$\alpha\alpha\delta\delta$-tetraphenylacetylenyl-$\alpha\delta$-butylene glycol*, $HO\cdot C(C{:}CPh)_2\cdot CH_2\cdot CH_2\cdot C(C{:}CPh)_2\cdot OH$.

In addition, the preparation of an acetylenic-ethylenic alcohol and a glycol was attempted from magnesium phenylacetylenyl bromide and phenyl styryl ketone and dibenzoylethylene (Conant and Lutz, *J. Amer. Chem. Soc.*, 1923, **45**, 1303) respectively. In accordance with our previous experience of aromatic ketones, the reaction did not proceed satisfactorily, resinous products being obtained.

EXPERIMENTAL.

2 : 5 - *Diphenylacetylenyl* - 2 : 5 - *dimethyltetrahydrofuran.*—Three grams of $\alpha\theta$-diphenyl-$\gamma\zeta$-dimethyl-$\Delta^{\alpha\eta}$-octadi-inene-$\gamma\zeta$-diol were heated for 1 hour at 100° in a sealed tube with 9 grams of 60 per cent. sulphuric acid. From the liquid, diluted with an equal volume of water, ether extracted a faintly yellow, very viscous oil, b. p. 206—207°/0·5 mm. (Found : C = 88·22; H = 6·72. $C_{22}H_{20}O$ requires C = 88·00; H = 6·67 per cent.).

Diacetyl and Magnesium Phenylacetylenyl Bromide.—An ethereal solution of this Grignard reagent (prepared from 7·1 grams of phenylacetylene, 1 mol.) was added slowly to 4·78 grams of diacetyl (1 mol.) in ether, cooled in ice and salt. The mixture was boiled for 1 hour (if the boiling is omitted, the yield of ketol is diminished by one-half), and acidified with iced dilute sulphuric acid; ether then extracted, together with the glycol, the ketol *α-phenyl-γ-methyl-Δ^{α}-pentinene-γ-ol-δ-one*, a greenish-yellow liquid possessing a pleasant rose-oil odour and a burning taste, b. p. 120°/0·5 mm. (Found : C = 76·10; H = 6·59. $C_{12}H_{12}O_2$ requires C = 76·56; H = 6·38 per cent.). The *semicarbazone*, deposited from alcohol as a white powder, melted at 171—172° (Found : N = 16·93. $C_{13}H_{15}O_2N_3$ requires N = 17·14 per cent.).

Ethyl Oxalate and Magnesium Phenylacetylenyl Bromide.—3·65 Grams of the ester in dilute ethereal solution were gradually added to the Grignard reagent (from 10·2 grams of phenylacetylene, 4 mols.) in ether, cooled with ice and salt. The magnesium compound was decomposed with iced dilute acetic acid, and from the product ether removed *ααββ-tetraphenylacetylenylethylene glycol*, long, colourless prisms from alcohol, m. p. 147° (decomp.). Yield, 4·5 grams. The substance was soluble in chloroform or ether, insoluble in light petroleum, and decomposed suddenly with explosive rapidity on heating. For analysis, it was mixed with an equal volume of finely divided silica (Found : C = 88·51, 88·45; H = 4·75, 4·81. $C_{34}H_{22}O_2$ requires C = 88·31; H = 4·76 per cent.). Decomposition occurred when acetylation was attempted.

Ethyl Succinate and Magnesium Phenylacetylenyl Bromide.—This reaction was carried out as above, 4 mols. of the Grignard reagent to 1 mol. of the ester being used; the mixture was boiled for 1 hour before being worked up. The *ααδδ-tetraphenylacetylenyl-αδ-butylene glycol* was recrystallised first from a mixture of chloroform and light petroleum and then from alcohol, from which it separated in lustrous leaflets. These contained 1 mol. of alcohol of crystallisation which was expelled on heating in the steam-oven;

the glycol then melted at 134—136° (Found : C = 87·98; H = 5·27. $C_{36}H_{26}O_2$ requires C = 88·16; H = 5·31 per cent.).

In conclusion, we wish to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant which has enabled one of us (W. M. H.) to take part in this investigation. We desire also to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the expenses of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

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CCIV.—*A Criticism of the Distillation Method of Measuring Vapour Pressure.*

By LAWSON JOHN HUDLESTON.

DUNN and RIDEAL (this vol., p. 676) describe the determination of the partial vapour pressure of hydrogen chloride over hydrochloric acid solution by means of the distillation method and find that the deduced values for the activity of hydrogen chloride in the solution do not agree, at high concentration, with those calculated from *E.M.F.* data. This discrepancy may be due to a fallacy in the fundamental theory on the basis of which the first case was discussed. In effect, the apparatus consisted of a flask of hydrochloric acid, kept at 25°, connected to another, kept at 0°, in which a distillate of very dilute acid collected, the flasks and connecting tubes containing only the vapour from the solution. It was assumed that the molecular ratio of hydrogen chloride to water in the distillate condensing was equal to the ratio of p_{HCl} to p_{H_2O}, the partial vapour pressures above the acid at 25°. This may not be true. Near each liquid surface the partial pressures appropriate to the temperature and concentration will be practically maintained and *the excess quantities of water and hydrogen chloride arriving at the cooler surface will be condensed.* For a pure liquid, the rate of passage from a hot to a cold zone is some function of *the difference between the pressures concerned*, $f(p - p')$, and it may be that, at the low pressure (maximum 23 mm.) of the experiments under consideration, this will be partly true for each component separately. If so, the partial pressures over the cold solution being denoted by p'_{HCl} and p'_{H_2O} the molecular ratio of the substances arriving at the cold surface, and therefore the composition

of the distillate condensing, will be $f(p_{HCl} - p'_{HCl})/f(p_{H_2O} - p'_{H_2O})$. This is equivalent to the former assumption only if

$$f(p_{HCl} - p'_{HCl})/p_{HCl} = f(p_{H_2O} - p'_{H_2O})/p_{H_2O}. \quad \text{(I.)}$$

No experimental figures, unmodified by calculation, are given, but it can readily be shown from other data that the concentration of hydrogen chloride in the distillate in all the cases considered is very small compared with that in the original solution and consequently p'_{HCl} is negligibly small compared with p_{HCl}. On the contrary, p'_{H_2O} is never sensibly different from 4·6 mm., the vapour pressure of pure water at 0°, and this is 20 per cent. of p_{H_2O} for the dilute solutions and 27 per cent. of p_{H_2O} when $c = 5$ (Dobson and Masson, this vol., p. 668). With this difference in the "back-pressures" of the two components, (I) is not likely to be true.

The quantitative effect of this correction depends on the nature of the undefined function. Even if it be simple proportionality, the factors in the two cases may not be the same owing to the difference in molecular weight. The effect of the "back-pressure" will be to reduce the amount of water condensing; the original calculation, therefore, should give too high values for the vapour pressure.

It may be that the hydrogen chloride does not pass by virtue of its own distillation (the function may be of such a form that distillation at so low a pressure is negligible), but is carried along mechanically by the water vapour as by the air in the streaming method. If so, the lower the total pressure and the slower the rate of distillation the less likely is the vapour to move as a whole, so that these experiments should give too low results. Possibly the two effects are to some extent superimposed. Where so much is uncertain it would be profitless to attempt a quantitative correction, but it is clear that the method, under these conditions, does not provide a certain means for measuring partial vapour pressures. The question could easily be tested experimentally by varying the *temperature* of the condenser (and thus p'_{H_2O}) and observing whether the composition of the distillate is affected.

THE EDWARD DAVIES LABORATORIES,
UNIVERSITY COLLEGE, ABERYSTWYTH. [*Received, May 5th*, 1924.]

CCV.—*Electrical Conductivities of Mixtures of Aniline, Acetic Acid, and Water.*

By JAMES ROBERT POUND.

WHILE the materials used in the determinations of the densities and viscosities of mixtures of aniline, acetic acid, and water (Pound and Russell, this vol., p. 769) were available, it was thought desirable to measure the electrical conductivities of those mixtures.

The acetic acid used in the present work was rendered anhydrous by freezing it twice and distilling it through a fractionating column after a day's contact with phosphorus pentoxide, the first fraction and a considerable residue being rejected. It is possible that the acetic acid used in the previous work was not anhydrous; those results and conclusions, however, would be little affected thereby. The densities, contractions, and viscosities of mixtures of aniline and the distilled, anhydrous acetic acid were determined at 30°; the results, given in Table VII, supplement those of the previous paper. The electrical conductivities were measured by the usual Kohlrausch method, the electrolytic cells being standardised with potassium chloride solutions. The electrical conductivities, given in the usual ohm/cm. units, have only a moderate degree of accuracy, say $\pm 0{\cdot}005$; four significant figures are given usually, but the last figure is of little importance.

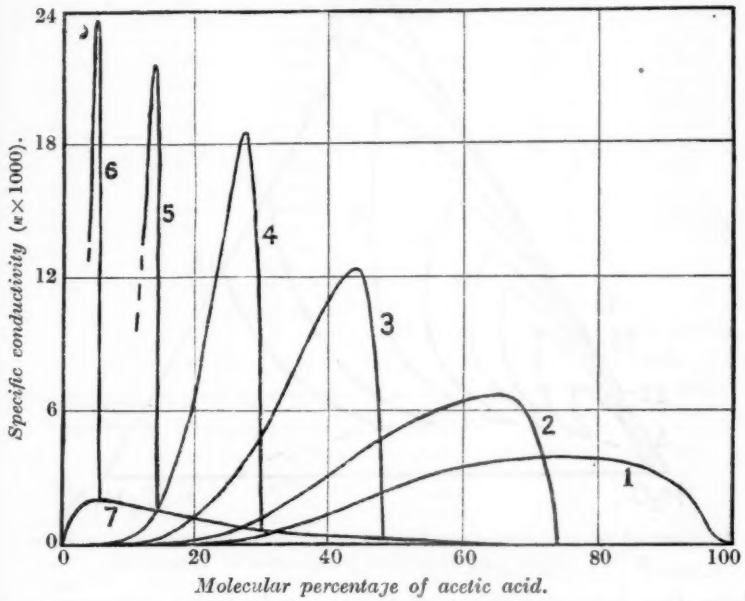
The electrical conductivities were found for mixtures of aniline with (1) 100 per cent. acetic acid and with (2) 90·36, (3) 75·70, (4) 58·46, (5) 36·625, and (6) 16·320 weight per cent. acetic acid solutions in water. The strengths of the aqueous acid solutions were determined by titration with baryta water. The solutions (2), (3), and (4) were those used in the previous work, whilst the solutions (5) and (6) were made up from the distilled acetic acid and water. The conductivities of these acetic acid solutions agree with the results of other observers. The mixtures of these acids with the aniline were made up by weight. In the tables are given the percentage molecules of aniline and of acetic acid, the molecular percentage of water being found by difference. Mixtures of aniline with the concentrated acetic acids (1), (2), and (3), containing less than about 40 weight per cent. of aniline, developed a light pink colour; this colour was more pronounced and less transient with the mixtures containing the smaller amounts of aniline. In Fig. 1 the conductivities of the mixtures of aniline with the (100 per cent.) acetic acid and with the five acetic acid solutions are shown by the curves (1) to (6), and curve (7) shows the conductivities of mixtures of acetic acid and water; and in Fig. 2 the values are set to triangular

co-ordinates; in both graphs, the molecular percentage compositions are used for reference.

It will be seen that the mixtures having good conductivity are, in general, those showing the greatest contraction and having the greatest viscosity (see previous paper); but the mixtures of greatest conductivity contain large proportions of water. The mixture of maximum conductivity, 0·024 unit approximately, contains about 92 mol. per cent. of water, 5 mol. per cent. of acetic acid and 3 mol. per cent. of aniline, whilst the mixture of maximum viscosity

FIG. 1.

Specific conductivities of mixtures of aniline, acetic acid, and water at 30°.

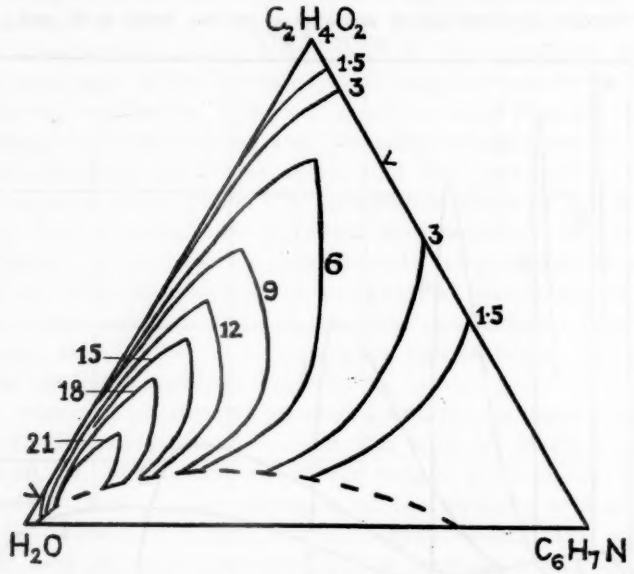


contains no water and that of maximum contraction is of intermediate composition. Compound formation in solution, as indicated by the viscosities and contractions of the solutions, is accompanied by tendency to ionisation, which, however, is especially favoured by the presence of water. The best conducting mixtures are obtained by adding small amounts of aniline to acetic acid–water solutions and especially to such of low acid content. The mobilities of the ions, which are related in some way to the fluidities of the solutions, also increase as the water content increases, and this too favours good conducting mixtures of large water content.

The presence of much aniline means a poorly conducting mixture,

and aniline and water alone give mixtures having low conductivity. There seem to be two types of conducting dilute solutions. When the conductivity, κ, of the solution is plotted as the ordinate and the weight (or molecular) percentage, w, of the solute or minor component is plotted as the abscissa, the one class of solutions gives κ–w curves that are concave to the axis of abscissæ but become straight lines when they approach the zero point, the conductivity of the pure solvent being practically zero. Aqueous solutions of salts, acids, and bases are the chief examples of this type; for

FIG. 2.



Mixtures of equal electrical conductivities of aniline, acetic acid, and water at 30°; 1000 κ and molecular percentages of components.

them the molecular (or equivalent) conductivity increases with dilution and tends towards a finite limit at infinite dilution. The other class of solutions gives κ–w curves that are convex to the axis of abscissæ and do not become straight lines as they approach the zero point; for them the molecular conductivity decreases with dilution continuously, that is, the conductivity decreases always more rapidly than the concentration (or percentage weight) of the solute (or minor component). Solutions of acetic acid or of acetic acid plus water in aniline, and solutions of sulphuric acid or of sulphuric acid plus water in ether are of this type. Probably in the first or aqueous-solution type ionisation is predominant, although it may be preceded by complex formation, but in the

latter type of solutions complex formation is predominant and is followed by only slight ionisation. There are other differences between the two types of solutions, for example, dilute solutions of sulphuric acid in ether do not act on iron and zinc, that is, they are

Specific Conductivities at 30° of Mixtures of Aniline, Acetic Acid, and Water.

TABLE I.

Mixtures of aniline and 100 per cent. acetic acid.

Aniline. Mol. %.	Acetic Acid. Mol. %.	$\kappa \times 10^3$.
0	100	0·00008
2·295	97·705	0·2042
3·457	96·543	0·5610
7·193	92·807	2·247
14·64	85·36	3·732
20·605	79·395	3·880
25·733	74·267	3·644
26·455	73·545	3·662
29·81	70·19	3·843
47·68	52·32	2·757
58·455	41·545	1·550
71·92	28·08	0·2645
84·663	15·337	0·01356
100	0	<0·00001

TABLE II.

Mixtures of aniline and 90·36 per cent. acetic acid.

0	73·77	0·04233
5·635	69·615	5·694
11·755	65·101	6·703
19·377	60·225	6·294
27·27	53·67	5·544
43·63	41·59	3·583
69·586	22·415	0·2668

TABLE III.

Mixtures of aniline and 75·70 per cent. acetic acid.

0	48·315	0·2030
2·065	47·315	6·860
4·325	46·225	10·25
9·515	43·720	12·26
14·675	41·225	11·36
20·65	38·335	10·05
31·995	32·855	6·92
52·505	22·945	1·993
70·15	14·42	0·1541
82·051	8·671	0·01074
89·621	4·998	0·00170

TABLE IV.

Mixtures of aniline and 58·46 per cent. acetic acid.

Aniline. Mol. %.	Acetic Acid. Mol. %.	$\kappa \times 10^3$.
0	29·69	0·628
0·973	29·401	7·295
2·267	29·016	12·30
3·512	28·65	15·22
7·07	27·59	18·30
12·36	26·02	16·84
18·55	24·18	13·81
32·75	19·97	7·06
56·42	12·94	0·9225
75·10	7·39	0·03433

TABLE V.

Mixtures of aniline with 36·625 per cent. acetic acid.

0	14·776	1·505
1·435	14·565	14·00
2·768	14·369	19·05
6·235	13·856	21·20
10·395	13·242	20·56
15·660	12·464	14·82
20·954	11·682	10·79
74·842	3·718	0·01911
Aniline saturated with water.		>0·0001

TABLE VI.

Mixtures of aniline with 16·320 per cent. acetic acid.

0	5·528	2·001
0·478	5·502	9·294
1·083	5·468	15·94
2·436	5·393	23·32
4·458	5·282	23·57
81·619	1·016	0·0020
Distilled water.		0·0049
Water saturated with aniline.		0·0071

TABLE VII.

Densities, Contractions, and Viscosities at 30° of Mixtures of Aniline and (100 per cent.) Acetic Acid.

Aniline. Wt. %.	$d_4^{30°}$.	Contr. (c.c. per 100 c.c.).	Visc. (C.G.S. units).	Aniline. Wt. %.	$d_4^{30°}$	Contr. (c.c. per 100 c.c.).	Visc. (C.G.S. units).
0	1·03779	0	0·01031	39·705	1·08029	4·856	0·1623
28·693	1·08426	4·950	0·1371	58·558	1·06071	3·537	—
35·805	1·08243	4·943	0·1604	100	1·01310	0	0·03226

not " acid solutions " or they do not contain many hydrogen-ions and are thus distinct from solutions of the acid in water. Decrease of molecular conductivity with dilution has been correlated with solvents of low dielectric constant, as are aniline and acetic acid. However, much work on the electrical conductivities of " dilute solutions " deals with far more dilute solutions than those investigated by and referred to by the author. The object of the present work was to study, not so much dilute solutions, as the complete set of ternary mixtures. The main conclusion of this work is that the ternary mixtures in which complex formation is prominent are also mixtures of good conductivity, and of these the more aqueous are the better conductors.

THE SCHOOL OF MINES, BALLARAT,
VICTORIA.

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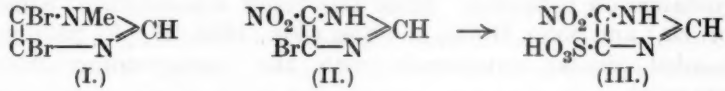
CCVI.—*The Bromo-derivatives of* 1-*Methylglyoxaline, and the Constitution of "Chloroxalmethylin."*

By ISIDORE ELKANAH BALABAN and FRANK LEE PYMAN.

THE bromination of 1-methylglyoxaline takes a similar course to that of glyoxaline itself (Balaban and Pyman, J., 1922, **121**, 947), 2 : 4 : 5-tribromo-1-methylglyoxaline being the main product of the reaction; a little 4 : 5-*dibromo*-1-*methylglyoxaline* (I) is formed, of which the constitution follows from the preparation of the substance by the methylation of 4 : 5-dibromoglyoxaline. On the other hand, 2 : 4 : 5-tribromo-1-methylglyoxaline is much more resistant to reduction by sodium sulphite than the unmethylated base, and therefore does not serve as a source of either 4- or 5-bromo-1-methylglyoxaline. These bases are obtained simultaneously by methylation of 4(or 5)-bromoglyoxaline with methyl sulphate, and 5-*bromo*-1-*methylglyoxaline* may be prepared conveniently in this way, but the yield of 4-*bromo*-1-*methylglyoxaline* is very small. A possible method of preparing this substance was suggested by the

facts (1) that the 4(or 5)-chloro-1-methylglyoxaline prepared by Wallach (*Annalen*, 1877, **184**, 121) by the action of phosphorus pentachloride on *sym*-dimethyloxamide has been stated by Sarasin (*Helv. Chim. Acta*, 1923, **6**, 370) to be 4-chloro-1-methylglyoxaline, and (2) that Wallach (*Annalen*, 1882, **214**, 193) obtained a basic compound by the action of phosphorus pentabromide on *sym*-diethyloxamide. It was found, however, (1) that the only isolable product of the interaction of phosphorus pentabromide and *sym*-dimethyloxamide was 4 : 5-dibromo-1-methylglyoxaline, and (2) that Sarasin had incorrectly deduced the constitution of Wallach's 4(or 5)-chloro-1-methylglyoxaline, which is in fact 5-chloro-1-methylglyoxaline.* Sarasin showed that on distilling the methiodide of this base an isomeric base is obtained which yields the same methiodide. He regarded this as 5-chloro-1-methylglyoxaline, but in view of our results it is clearly 4-chloro-1-methylglyoxaline. It therefore appeared that the distillation of the methiodide of 5-bromo-1-methylglyoxaline [4(or 5)-bromo-1 : 3-dimethylglyoxalinium iodide] should yield mainly 4-bromo-1-methylglyoxaline, and this proved to be the case.

In seeking for methods of determining the orientation of the 4(and 5)-bromo-1-methylglyoxalines, the reactivity of the halogen atom in 4(or 5)-bromoglyoxaline was first examined. This substance does not undergo condensation with bromobenzene when treated with either sodium or molecular copper in ethereal solution, or with sodium in boiling xylene, but can be recovered to the extent of about 90 per cent. unchanged. The halogen atom may be replaced by hydrogen by means of hydriodic acid and phosphorus at 160°, but no evidence of the formation of either glyoxaline or of glyoxaline-4-sulphonic acid was obtained when 4-bromoglyoxaline was heated with 20 per cent. aqueous sodium sulphite for 6 hours at 160—170°, 69 per cent. being recovered unchanged. The reactivity of the halogen atom is increased by the introduction of a nitro-group into the ortho-position, for 4(or 5)-bromo-5(or 4)-nitroglyoxaline (II) gives 5(*or* 4)-*nitroglyoxaline*-4(*or* 5)-*sulphonic acid* (III) on boiling with sodium sulphite, although it could not be condensed with either



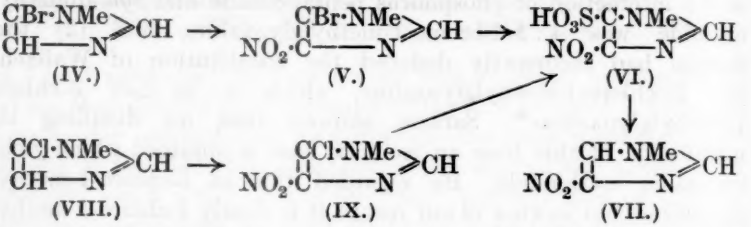
(I.) (II.) (III.)

ethyl sodiomalonate in alcohol at 100° or with potassium cyanide in boiling aqueous solution.

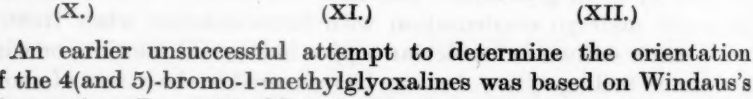
It was found that the halogen atom in the *nitro*-derivatives

* Since this paper was communicated to the Society, Sarasin and Wegmann (*Helv. Chim. Acta*, 1924, **7**, 713) have arrived at the same conclusion.

(V and IX) of 5-bromo-1-methylglyoxaline (IV) and 5-chloro-1-methylglyoxaline (VIII) (chloroxalmethylin) could be replaced similarly by the sulphonic acid residue, which gave place to hydrogen on hydrolysis, yielding 4-nitro-1-methylglyoxaline (VII) (Hazeldine, Pyman, and Winchester, this vol., p. 1431) and thus establishing the orientation of these bases directly and of 4-bromo-1-methylglyoxaline (X) indirectly.



The nitration product of this base, 4-*bromo*-5-*nitro*-1-*methylglyoxaline* (XI), is the main product of the methylation of 4(or 5)-bromo-5(or 4)-nitroglyoxaline (II). Both 4- and 5-bromo-1-methylglyoxaline readily yield *sulphonic acids*.



An earlier unsuccessful attempt to determine the orientation of the 4(and 5)-bromo-1-methylglyoxalines was based on Windaus's observation (*Ber.*, 1909, **42**, 758) that the condensation of 4-methylglyoxaline with formaldehyde leads to the introduction of the hydroxymethyl group into the 5-position, since the product yields 4 : 5-dimethylglyoxaline on reduction with hydriodic acid and phosphorus. It was thought that the 4(and 5)-bromo-1-methylglyoxalines would similarly yield 5(and 4)-hydroxymethyl derivatives, which would yield on reduction the known 1 : 4- and 1 : 5-dimethylglyoxalines respectively. Actually, 5-bromo-1-methylglyoxaline condensed with formaldehyde to yield 5-*bromo*-2-*hydroxymethyl*-1-*methylglyoxaline* (XII), which gave 1 : 2-dimethylglyoxaline on reduction. Since this result was obtained, Sarasin (*loc. cit.*) and Sonn, Hotes, and Sieg (*Ber.*, 1924, **57**, [*B*], 953) have recorded similar experiences with the corresponding chloro-compound.

Experimental.

Bromination of 1-*Methylglyoxaline.*—To 18 grams of 1-methylglyoxaline in 60 c.c. of chloroform, 36 grams of bromine in 60 c.c. of chloroform were added at 5—10° in the course of ½ hour. After the solvent had been removed in a current of steam, 2 : 4 : 5-tribromo-

1-methylglyoxaline separated on cooling and was purified by crystallisation from water (yield 10·4 grams). On extracting the acid filtrate with ether, 4 : 5-dibromo-1-methylglyoxaline was collected, and gave 0·49 gram of the pure picrate, whilst after concentrating the aqueous liquor, basifying with sodium hydroxide, and extracting with chloroform, 1-methylglyoxaline was recovered, from which 23·3 grams of the pure picrate were obtained.

2 : 4 : 5-Tribromo-1-methylglyoxaline crystallises from water in fine needles * and from ether in dense prisms which melt at 93—94·5° (corr.). Wyss (*Ber.*, 1877, **10**, 1373) and Wallach (*Ber.*, 1883, **16**, 537) both give m. p. 88—89° (Found : Br = 75·2. Calc., Br = 75·2 per cent.). It yields, with concentrated hydrochloric acid, a *hydrochloride* (prisms, m. p. 190—200°), which dissociates on addition of water. The base was recovered to the extent of 90 per cent. unchanged after boiling with sodium sulphite (1 mol.) in 20 per cent. aqueous solution for 5 hours, 4 : 5-dibromo-1-methylglyoxaline being isolated as picrate (yield * 1 per cent.).

4 : 5-*Dibromo*-1-*methylglyoxaline* (I) was also prepared (1) by heating 4 : 5-dibromoglyoxaline with methyl sulphate, and (2) by the interaction of *sym*-dimethyloxamide and phosphorus pentabromide after Wallach (*loc. cit.*) (yields 7 and 11 per cent. with 1 and 2 mols. of pentabromide, respectively). In all cases the product was isolated and identified as the picrate. The base crystallises from water in fine needles and from ether in large, rectangular prisms which melt at 79—80° (corr.) (Found : C = 20·0; H = 2·0; N = 11·9; Br = 66·6. $C_4H_4N_2Br_2$ requires C = 20·0; H = 1·7; N = 11·7; Br = 66·6 per cent.). It is very sparingly soluble in hot water, easily soluble in alcohol or ether, and less soluble in chloroform. The *hydrochloride* crystallises from 5*N*-hydrochloric acid in long, rectangular prisms which lose $2H_2O$ in a vacuum over sulphuric acid (Found : 11·9. Calc., 11·5 per cent.), and then melt to a clear liquid at 179° (corr.) after softening earlier. It is partly dissociated by water (Found : in salt dried in a vacuum, Cl = 12·7. $C_4H_4N_2Br_2,HCl$ requires Cl = 12·8 per cent.). The *nitrate* crystallises from dilute nitric acid in rectangular prisms, m. p. 153° (corr.) (Found : N = 14·2. $C_4H_4N_2Br_2,HNO_3$ requires N = 13·9 per cent.). The *picrate* crystallises from water in long, yellow needles, m. p. 148—149° (corr.). It is soluble in about 6 parts of hot alcohol or 30 parts of boiling water (Found : C = 25·6; H = 1·9; N = 14·9. $C_4H_4N_2Br_2,C_6H_3O_7N_3$ requires C = 25·6; H = 1·5; N = 14·9 per cent.).

Methylation of 4(*or* 5)-*Bromoglyoxaline.*—Eighteen grams of

* The substances described in this paper were colourless, and yields refer to pure compounds in per cent. of theoretical, unless otherwise stated.

the base were stirred with 12 c.c. of methyl sulphate (in three tubes), cooling in running water, until a vigorous reaction had taken place. After heating for 15 minutes in boiling water, the product was mixed with aqueous sodium hydroxide and extracted with ether (extract A). The liquor was acidified, basified with sodium carbonate, and extracted with ether, which removed 2·5 grams of 4(or 5)-bromoglyoxaline, m. p. 131—132°. The oily residue A was mixed with 20 grams of picric acid in 300 c.c. of hot alcohol, and gave at once 24·4 grams of pure 5-bromo-1-methylglyoxaline picrate, then mixtures which gave on fractional crystallisation from alcohol 0·71 gram of pure 4-bromo-1-methylglyoxaline picrate, whilst the mixed bases regenerated from the final mother-liquors amounted to only 0·2 gram. The direct yields of the two isomerides are thus 51 and 1·5 per cent. of the theoretical, respectively, the ratio being 34 : 1.

5-Bromo-1-methylglyoxaline (IV) distils at 128°/*ca.* 15 mm., and sets to a hard mass of needles, m. p. 45—46° (corr.) (Found : C = 29·8; H = 3·4; N = 17·4; Br = 49·5. $C_4H_5N_2Br$ requires C = 29·8; H = 3·1; N = 17·4; Br = 49·7 per cent.). It is deliquescent and very easily soluble in water or the usual organic solvents except light petroleum. The *hydrochloride* crystallises from water in long, glistening needles, which lose $\frac{1}{2}H_2O$ at 100° (Found : 4·3. Calc., 4·3 per cent.), and then melt at 155° (corr.). It is easily soluble in water (Found : in dried salt, Cl = 18·0. $C_4H_5N_2Br,HCl$ requires Cl = 18·0 per cent.). The *nitrate* separates from water in irregular prisms which are anhydrous and melt and effervesce at 155° (corr.). It is soluble in 4 parts of boiling water (Found : C = 21·3; H = 3·0; N = 19·0. $C_4H_5N_2Br,HNO_3$ requires C = 21·4; H = 2·7; N = 18·7 per cent.). The *hydrogen oxalate* crystallises from water in silky needles, which lose nearly $\frac{1}{2}H_2O$ in a vacuum over sulphuric acid (Found : 2·3. Calc., 3·5 per cent.), and then melt at 147° (corr.) after previous sintering. It is readily soluble in warm water (Found, in salt dried in a vacuum : C = 28·1; H = 3·1. $C_4H_5N_2Br,C_2H_2O_4$ requires C = 28·6; H = 2·8 per cent.). The *picrate* crystallises from alcohol in glistening, yellow needles, which are anhydrous, melt at 190° (corr.), and are very sparingly soluble in water or alcohol (Found : C = 30·5; H = 2·4; N = 18·1. $C_4H_5N_2Br,C_6H_3O_7N_3$ requires C = 30·8; H = 2·0; N = 17·9 per cent.).

The sulphonation and nitration of 5-bromo-1-methylglyoxaline were effected by methods similar to those employed for 4-bromoglyoxaline (Balaban and Pyman, *loc. cit.*), giving the following derivatives :

5-Bromo-1-methylglyoxaline-4(?)-sulphonic acid (yield 78 per cent.). It crystallises from water in irregular prisms which melt at 284°

(corr.) after drying at 120°, and is soluble in 55 parts of boiling water, but almost insoluble in cold water (Found : C = 19·9; H = 2·3; N = 11·6; Br = 33·4; S = 13·1. $C_4H_5O_3N_2BrS$ requires C = 19·9; H = 2·1; N = 11·6; Br = 33·2; S = 13·3 per cent.). After heating 0·38 gram of the acid with 5 c.c. of 30 per cent. aqueous sulphuric acid for 3 hours at 170°, 0·11 gram of 5-bromo-1-methylglyoxaline picrate was isolated.

5-Bromo-4-nitro-1-methylglyoxaline (V) (yield 80 per cent.). It crystallises from water in long, silky needles, m. p. 180° (corr.) and is soluble in 85 parts of boiling water, but dissolves only very sparingly in cold water. It is sparingly soluble in hot alcohol, moderately soluble in benzene or chloroform, and almost insoluble in ether (Found : C = 23·0, 23·1; H = 2·0, 2·2; N = 20·7; Br = 38·9. $C_4H_4O_2N_3Br$ requires C = 23·3; H = 1·9; N = 20·4; Br = 38·8 per cent.). It is insoluble in alkalis, but dissolves in 5*N*-hydrochloric acid, yielding a sparingly soluble *hydrochloride*, which melts at about 155° and yields the base on treatment with water. The base crystallises unchanged from aqueous picric acid.

4-Nitro-1-methylglyoxaline-5-sulphonic Acid (VI).—Three grams of 5-bromo-4-nitro-1-methylglyoxaline were boiled under reflux with 16·5 c.c. of 20 per cent. aqueous sodium sulphite (1 mol.) for 3 hours. After keeping, 0·51 gram of unchanged material separated (m. p. 180°) and a further 0·2 gram was recovered by extraction with chloroform. The liquor was mixed with hydrochloric acid and concentrated, when mixtures of the sulphonic acid with sodium chloride were obtained, which gave the pure acid (about 1 gram) after recrystallisation from dilute hydrochloric acid. It forms flat, irregular prisms which are anhydrous and melt and decompose at 254° (corr.). It is readily soluble in water, but insoluble in absolute alcohol (Found : C = 23·3; H = 2·6; N = 20·6; S = 15·4. $C_4H_5O_5N_3S$ requires C = 23·2; H = 2·4; N = 20·3; S = 15·4 per cent.). The *sodium* salt crystallises from hot alcohol, in which it is very sparingly soluble, in fine needles.

Hydrolysis of the Sulphonic Acid.—0·65 Gram was heated with 5 c.c. of 30 per cent. aqueous sulphuric acid for 3 hours at 170°. After addition of alkali, chloroform removed 0·08 gram of 4-nitro-1-methylglyoxaline, melting at 134° alone or mixed with an authentic specimen, and identified also by analysis (Found : C = 37·6; H = 4·0. Calc., C = 37·8; H = 3·9 per cent.).

5-Bromo-2-hydroxymethyl-1-methylglyoxaline (XII).—3·84 Grams of 5-bromo-1-methylglyoxaline and 11·5 c.c. of 40 per cent. aqueous formaldehyde were heated for 6 hours at 130°. The product was evaporated to a syrup, mixed with hydrochloric acid and concentrated, when the crude hydrochloride separated and gave the pure

base (yield 42 per cent.) on basification with sodium carbonate. It crystallised from water in dense, waxy, anhydrous rhomboids, m. p. 143° (corr.). It is soluble in 15 parts of boiling water (Found: N = 14·9; Br = 41·4. $C_5H_7ON_2Br$ requires N = 14·7; Br = 41·9 per cent.). The *picrate* crystallises from alcohol in long, yellow, anhydrous needles, m. p. 165—166° (corr.). It is very sparingly soluble in alcohol (Found: N = 16·8. $C_5H_7ON_2Br,C_6H_3O_7N_3$ requires N = 16·7 per cent.).

Reduction.—One gram of the above base, 2·5 c.c. of hydriodic acid (*d* 1·7), and 0·3 gram of red phosphorus were heated for 6 hours at 160°. After basifying, ether extracted 0·7 gram of oil, which was converted into picrate, when 0·39 gram of pure 1 : 2-dimethylglyoxaline picrate was obtained, melting at 181° (corr.) alone or mixed with a specimen prepared by the methylation of 2-methylglyoxaline (Jowett and Potter, J., 1903, **83**, 464, who give m. p. 179°).

4(*or* 5)-*Bromo*-1 : 3-*dimethylglyoxalinium iodide*, prepared by warming either 4- or 5-bromo-1-methylglyoxaline with methyl iodide under reflux, crystallises from alcohol in prismatic rods which are anhydrous, melt at 202—204° (corr.), and are readily soluble in water or in 8 parts of hot alcohol (Found: I = 41·7. $C_5H_8N_2BrI$ requires I = 41·9 per cent.).

Distillation.—Ten grams of the methiodide were distilled under 15 mm. from an oil-bath at 235°. The distillate (yield 94 per cent.) was crystallised as nitrate, when 3·2 grams of pure 4-bromo-1-methylglyoxaline nitrate were obtained (yield 43 per cent.), and its identity was confirmed by the preparation of the picrate. Separation of the residual mixture of 4- and 5-bromo-1-methylglyoxalines proved very difficult, and eventually it was nitrated, when the presence of 5-bromo-1-methylglyoxaline in the mixture was proved by the isolation of its 4-nitro-derivative (0·33 gram, m. p. 180°), through its sparing solubility in ether.

4-*Bromo*-1-*methylglyoxaline nitrate* crystallises from dilute nitric acid in anhydrous, rectangular prisms, m. p. 155° (corr.). It is soluble in about 3 parts of boiling water (Found: C = 21·4; H = 2·9. $C_4H_5N_2Br,HNO_3$ requires C = 21·4; H = 2·7 per cent.).

The *picrate* crystallises from alcohol in long, yellow, anhydrous, prismatic needles, m. p. 179° (corr.). It is soluble in 7 parts of hot alcohol (Found: C = 30·8; H = 2·3; N = 18·1; Br = 20·2. $C_4H_5N_2Br,C_6H_3O_7N_3$ requires C = 30·8; H = 2·0; N = 17·9; Br = 20·5 per cent.).

The base was obtained as an oil, which did not crystallise. Its sulphonation and nitration by methods similar to those employed for 4-bromoglyoxaline gave the following products :

4-*Bromo*-1-*methylglyoxaline*-5(?)-*sulphonic acid* (yield 77 per cent.). It crystallises from water in long, rectangular prisms, which contain $1H_2O$ and melt and decompose at 256° (corr.). It is soluble in 15 parts of boiling water, but very sparingly soluble in cold water (Found, in acid dried at 120° : C = 19·7; H = 2·3. $C_4H_5O_3N_2BrS$ requires C = 19·9; H = 2·1 per cent. Found, in air-dried acid : H_2O = 7·0; Br = 31·0; S = 12·1. $C_4H_5O_3N_2BrS,H_2O$ requires H_2O = 6·9; Br = 30·9; S = 12·3 per cent.). After heating 0·35 gram with 5 c.c. of 30 per cent. aqueous sulphuric acid for 3 hours at 170°, the product gave 0·39 gram of 4-bromo-1-methylglyoxaline picrate, m. p. 178—179°.

4-*Bromo*-5-*nitro*-1-*methylglyoxaline* (XI) (yield 54 per cent.). It crystallises from water in glistening needles, m. p. 105° (corr.), which are soluble in 40 parts of boiling water, much less soluble in cold water, but readily soluble in alcohol, ether, or chloroform (Found : C = 23·1; H = 2·0; Br = 39·0. $C_4H_4O_2N_3Br$ requires C = 23·3; H = 1·9; Br = 38·8 per cent.). It is insoluble in alkalis, but dissolves in 5*N*-hydrochloric acid, giving a solution from which the base is precipitated on dilution with water.

Methylation of 4(*or* 5)-*Bromo*-5(*or* 4)-*nitroglyoxaline*.—Seven grams of this base were heated with 3·5 c.c. of methyl sulphate for 1 hour in boiling water. On mixing the product with aqueous sodium hydroxide and extracting with chloroform, 1·7 grams of nearly pure 4-bromo-5-nitro-1-methylglyoxaline were obtained, m. p. 98°, alone or in admixture with the pure compound. On recrystallisation, however, the melting point could not be raised above 100°, probably owing to the presence of a small proportion of the more sparingly soluble 5-bromo-4-nitro-1-methylglyoxaline. Its composition was further confirmed by analyses (C,H,N,Br). The original sodium hydroxide extract gave 1·4 grams of unchanged material when acidified.

Action of Sodium Sulphite on 4(*or* 5)-*Bromo*-5(*or* 4)-*nitroglyoxaline*. —Three grams of the base and 37·5 c.c. of 20 per cent. aqueous sodium sulphite (2 mols.) were boiled under reflux for 4 hours. The product was acidified with hydrochloric acid, and concentrated, the crude sulphonic acid being purified by recrystallisation from strong hydrochloric acid (yield 88 per cent.). 4(*or* 5)-*Nitroglyoxaline*-5(*or* 4)-*sulphonic acid* crystallises from dilute hydrochloric acid in irregular prisms which are anhydrous, and decompose at 300° (corr.) (Found : C = 18·4; H = 1·7; N = 21·8; S = 16·3. $C_3H_3O_5N_3S$ requires C = 18·7; H = 1·5; N = 21·8; S = 16·6 per cent.). It is readily soluble in water, but insoluble in absolute alcohol. The *sodium* salt is very sparingly soluble in alcohol, from which it crystallises in fine, colourless needles.

5-Chloro-1-methylglyoxaline, "Chloroxalmethylin," was prepared by Wallach's method (*loc. cit.*). Yield 48 per cent. A mixture of 5·3 grams of the *nitrate* [long, rectangular prisms from dilute nitric acid, m. p. 145° (corr.) (Found: C = 26·9; H = 3·6. $C_4H_5N_2Cl,HNO_3$ requires C = 26·7; H = 3·3 per cent.)] and 15 c.c. of concentrated sulphuric acid was heated for 1½ hours in boiling water, and then poured into water, when *5-chloro-4-nitro-1-methylglyoxaline* (IX) separated (yield 71 per cent.). It crystallises from water in fine needles, m. p. 147° (corr.), which are soluble in 40 parts of boiling water (Found: C = 29·5; H = 2·5; Cl = 22·0. $C_4H_4O_2N_3Cl$ requires C = 29·7; H = 2·5; Cl = 22·0 per cent.).

3·2 Grams boiled under reflux with 25 c.c. of 20 per cent. aqueous sodium sulphite for 5 hours gave, after working up as in the analogous case on p. 1569, 4-nitro-1-methylglyoxaline-5-sulphonic acid (yield 60 per cent.), which melted at 254° (corr.) alone or mixed with the substance prepared from the bromo-analogue and sodium sulphite, and similarly gave 4-nitro-1-methylglyoxaline (m. p. 134°) on hydrolysis.

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CCVII.—*The Electrometric Titration of Chromic Acid using* (a) *the Hydrogen Electrode, and* (b) *the Oxygen Electrode.*

By HUBERT THOMAS STANLEY BRITTON.

ON the assumption that each molecule of chromic acid contains two atoms of chromium, the conductivity of aqueous solutions of this compound (Walden, *Z. physikal. Chem.*, 1888, **2**, 49), coupled with the depression of freezing point exhibited by a half-molar solution, indicates, according to Ostwald (*ibid.*, p. 78), that the ions are Cr_2O_7'' and $2H^{\cdot}$. It is true that the equivalent conductivity of chromic acid increases only slightly with dilution, but this may be due to the relatively small value of the second dissociation constant. This view is borne out by the present investigation, which points, however, to the negative ion of the acid being CrO_4''.

Several workers, Sherrill and collaborators (*J. Amer. Chem. Soc.*, 1907, **29**, 1641), Spitalsky (*Z. anorg. Chem.*, 1907, **54**, 265), and Beck and Stegmüller (*Arbeit. K. Gesundheitsamt*, 1910, **34**, 4), have studied the probable simple dibasicity of chromic acid and have carried out experiments to determine its second dissociation constant. All their methods, however, involve certain assumptions and

cannot be regarded as supplying anything more than indirect, and consequently uncertain, proof of the actual nature of chromic acid.

The conductometric titrations of Miolati and Marcetti (*Gazzetta*, 1901, **31**, i, 116), the "glass cell" measurements of Hughes (*J. Amer. Chem. Soc.*, 1922, **44**, 2860), and the hydrogen electrode titration of Margaillan (*Compt. rend.*, 1913, **157**, 994) all give qualitative but definite evidence of the true mode of dissociation of chromic acid. Unfortunately, Margaillan published his results in the form of an inadequate diagram, and consequently efforts have been made to repeat his work in order to obtain quantitative results.

The Hydrogen Electrode.

It is generally stated that the hydrogen electrode is inapplicable in solutions containing reducible substances, such as nitrates and chlorates. Numerous attempts made by the author to use it in presence of chromates were unsuccessful, but true hydrogen-ion concentrations could be deduced when certain precautions were taken and the hydrion concentration was small—not greater than 10^{-3}.

The catalytic reduction of chromic acid in presence of platinum black appeared to depend on four main factors, namely, (1) the rate of passage of the hydrogen, (2) the position of the electrode with respect to the surface of the solution, (3) the surface of the platinum foil, and (4) the nature of the platinum-black deposit. With the majority of the electrodes used, variations in the rate at which the hydrogen was passed gave unsteady and low *E.M.F.'s*. These *E.M.F.'s* tended to approach the true value when the gas was passed very slowly, but even then the voltage oscillated as each bubble of hydrogen left the electrode vessel or on the slightest agitation. If, however, the electrode was formed of a sufficiently large piece of platinum foil, say 3 cm. × 1 cm., and not of wire,* a steady voltage, which was not much less than the true value, was slowly attained when the electrode was completely immersed in perfectly still solution. The *E.M.F.* fell immediately the solution was disturbed. When the foil was partly immersed and the hydrogen passed rapidly, the voltage fell very quickly and the direction of the current in the hydrogen–calomel combination became reversed, the potential difference approaching that obtained with an electrode of bright platinum. Thus it appears that the fineness of the particles of the platinum-black deposit was causing the hydrogen to be removed from the electrode, the more completely when the rate of passing the hydrogen was increased.

* Wire electrodes were found useless, since their hydrogen was readily discharged by chromic acid.

Electrodes having deposits of platinum black, varying in size of grain, were prepared by altering such factors as current density and acidity of the platinising solutions. These electrodes, however, did not give the anticipated measure of success and further experiments were made using lead acetate in the platinising solution. The author's experience, in contrast with that of Ellis (*J. Amer. Chem. Soc.*, 1916, **38**, 737), is that electrodes containing lead are the more satisfactory, and when they are used in chromic acid solutions the presence of the lead seems to be a distinct advantage —probably in rendering the particles of the platinum-black deposit coarser. These electrodes, although giving satisfactory results in solutions containing such reducible substances as nitrates and chromates, were not all that could be desired when free chromic acid was present. A really satisfactory electrode gives the same *E.M.F.* whether the saturated electrode is immersed in still liquid or whether the electrode is partly immersed and the solution is agitated by hydrogen emerging from the electrode. In practice, this may be regarded as a criterion of an efficient electrode. As the catalytic activity of the electrode appeared to be determined by the size of the particles of platinum black, it was thought that the surface of the platinum itself might play an important part, for a polished surface would tend to become smaller than a rough surface on platinisation. The surfaces of two platinum foil electrodes, lying on plate glass, were highly polished with a glass rod. A coarse, thin layer of platinum black was then deposited on each during 5 minutes, the current being reversed every half-minute. These electrodes were of the Hildebrand type (*J. Amer. Chem. Soc.*, 1913, **35**, 847) and were used together in the titration. One worked normally in the chromic acid solution and the other gave low results, varying with the rate of passage of the gas, but for values of p_H greater than 2·5 the second electrode indicated *E.M.F.'s* identical with those shown by the first electrode.

The Oxygen Electrode.

Seeing that the electrometric titration of chromic acid with the hydrogen electrode is not without difficulty and indeed involves some still unknown factors, it was decided to direct attention to the oxygen electrode. At the same time, the titration curve obtained by means of the hydrogen electrode would serve as a standard with which the oxygen electrode curves could be compared. Furman (*J. Amer. Chem. Soc.*, 1922, **44**, 2685; *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 79) has demonstrated the use of the oxygen and air electrodes in acidimetry and alkalimetry, especially in coloured solutions and also in presence of oxidising

agents. He points out that, although the oxygen electrode, owing to some irreversible process, does not assume a definite potential value in any given solution, the drift in potential difference is a small time effect only which does not in any way obscure the course of an ordinary titration. He claims that by employing an empirical scale against the *E.M.F.* readings a quantitative indication of the hydrion concentration may be obtained, with an accuracy of about half of a p_H unit. The observations of the author confirm in part these contentions. Some difficulty, however, in fixing the empirical scale arises for the following reasons: (1) any two similarly prepared platinum electrodes rarely indicate identical values in the same solution, (2) any one oxygen electrode does not give the same potential values in the same solution on any two successive occasions, (3) the *E.M.F.'s* recorded throughout a titration do not vary in harmony with those which would have been given by a hydrogen electrode, and (4) in order to assign an approximate empirical scale, it is essential to know the hydrion concentrations at two stages at least of the titration.

A plausible method of standardising an oxygen electrode is based on the oxygen–hydrogen cell. Thus if the *E.M.F.* of $\begin{matrix}\text{Pt}\\ \text{H}_2\end{matrix}\Big|$ solution $\Big|\begin{matrix}\text{sat. KCl}\\ \text{solution}\end{matrix}\Big|$ N-calomel be $-x$ volts, and the *E.M.F.* of $\begin{matrix}\text{Pt}\\ \text{O}_2\end{matrix}\Big|$ same solution as above $\Big|\begin{matrix}\text{sat. KCl}\\ \text{solution}\end{matrix}\Big|$ N-calomel be $+y$ volts, then the *E.M.F.* of the oxygen–hydrogen cell, $\begin{matrix}\text{Pt}\\ \text{O}_2\end{matrix}\Big|$ solution $\Big|\begin{matrix}\text{Pt}\\ \text{H}_2\end{matrix}$, is $x + y$ volts, which is usually equal to about 1·08 volts in all electrolytes. If the potential difference of the oxygen–hydrogen cell remained sufficiently constant, it would follow that the potential difference of the oxygen–N-calomel cell would always be more positive than the corresponding hydrogen–N-calomel cell by a definite amount. The magnitude of this amount, which may be peculiar to any given oxygen electrode, after being once determined would serve as a means of calibrating the electrode. The behaviour of the oxygen electrode is somewhat irregular and such a difference is not sufficiently constant throughout a titration. As the titration approaches the neutral point and then the alkaline zone, this difference generally becomes smaller and smaller. Usually this variation does not even take place uniformly, and in some cases it actually increases in the region of the neutral point and then decreases (*vide* Table III). If the hydrion concentration of the solution is known at the beginning and the end of a titration (say), then it is an easy matter to calculate by simple proportion an empirical hydrogen-ion scale covering the changes throughout the

whole titration (compare Fig. 2, scale for curve 1). The accuracy with which this scale responds to the change in hydrion concentration as shown by the oxygen electrode curve as compared with that shown by the hydrogen electrode is quite satisfactory.

Furman used an air electrode for the titration of an alkaline solution of sodium chromate against hydrochloric acid. It is surprising that he preferred to account for the two inflections in his titration diagram by the following equations :

$$\tfrac{1}{2}(H_2Cr_2O_7 + 2NaOH = Na_2Cr_2O_7 + 2H_2O),$$

and

$$\tfrac{1}{2}(Na_2Cr_2O_7 + 2NaOH = 2Na_2CrO_4 + H_2O).$$

Experimental.

1. *Titrations with the Hydrogen Electrode.*—Two hydrogen electrodes of the Hildebrand type (*J. Amer. Chem. Soc.*, 1913, **35**, 847), with platinum foil 3 × 1 cm. and ½ × 1½ cm., respectively, in area, were placed in 100 c.c. of 0·02475 *M*-chromic acid and connected to a cylinder of pure hydrogen. The solution to be titrated was linked up with a normal calomel electrode by saturated potassium chloride solution as junction liquid. The hydrogen and the calomel electrodes were connected to a potentiometer so that the potential difference between each hydrogen electrode and the calomel electrode could be measured. The electrodes were half immersed. Hydrogen was passed through the electrode vessels until equilibrium was attained, indicated by the steady *E.M.F.* obtained both when the hydrogen was passing and when it was stopped. One electrode (A) attained this state in about 15 minutes, whereas the other (B) failed to arrive at a true equilibrium value after an hour and gave values which varied with the rate of flow of the gas. In the initial stages of the titration reliance was placed on A only. After each addition of alkali (0·090*N*-sodium hydroxide) a rapid current of hydrogen was passed through the solution to ensure thorough mixing of the reactants. While a reading was being taken, the speed of the hydrogen was reduced to about two bubbles per second; this reading was checked by that taken when the hydrogen had been stopped. As titration proceeded, the difference between the *E.M.F.'s* given by electrode B when the hydrogen was passing and when it was stopped became less and less, and vanished when 17 c.c. of the alkali had been added ($p_H = 2$); thereafter the two electrodes behaved alike. The electrodes responded instantly to changes in hydrogen-ion concentration, but as a rule about 5 minutes were allowed for each reading. The level of the junction liquid was continually adjusted to that of the solution being titrated.

Results.—The voltages are given to the nearest millivolt, which is about the limit of accuracy obtainable with these electrodes in solutions containing no oxidising agents under the conditions prevailing in titration experiments.

TABLE I.

100 C.c. of 0·02475*M*-H_2CrO_4, titrated against 0·0900*N*-NaOH, using the hydrogen electrode against the *N*-calomel half-element. Temp. 18°.

NaOH (c.c.) ...	0·0	2·55	5·0	7·5	10·0	13·4	17·0
E.M.F.	0·377	0·379	0·380	0·384	0·389	0·394	0·399
NaOH (c.c.) ...	20·05	21·0	22·0	22·53	23·0	23·5	
E.M.F.	0·413	0·417	0·423	0·429	0·431	0·439	
NaOH (c.c.) ...	25·0	26·5	28·0	29·0	31·0	34·0	38·0
E.M.F.	0·460	0·477	0·568	0·588	0·605	0·626	0·637
NaOH (c.c.) ...	42·0	46·05	48·0	50·0	51·0	52·0	
E.M.F.	0·647	0·666	0·675	0·686	0·691	0·702	
NaOH (c.c.) ...	53·0	53·5	54·0	54·5	55·05	55·5	56·0
E.M.F.	0·720	0·727	0·746	0·779	0·857	0·897	0·914
NaOH (c.c.) ...	58·0	60·0	64·0	68·0	72·0	80·0	
E.M.F.	0·937	0·948	0·965	0·971	0·979	0·981	

These results are represented diagrammatically in Fig. 1. The scale of hydrogen-ion concentrations was obtained from the equation *E.M.F.* (obs.) = 0·283 + 0·0577 log 1/[H·].

The first section of the diagram shows the course of neutralisation of the strongly dissociated chromic acid to form sodium hydrogen chromate, $NaHCrO_4$, in solution, $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4'$, and the second shows the neutralisation of the extremely weakly dissociated $HCrO_4'$ anion to form sodium chromate.

Calculation from the *E.M.F.* given by the hydrogen electrode in 0·02475*M*-chromic acid solution shows that the degree of dissociation to the first stage at this dilution at 18° is about 95 per cent.

The second dissociation constant, $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$, is $4{\cdot}4 \times 10^{-7}$, the mean of eight values, obtained from different points on the curve, namely, 4·59, 3·76, 3·47, 5·17, 4·67, 4·56, 3·22, 5·28, each multiplied by 10^{-7}, which were calculated from the data obtained when 27·5, 31·0, 34·0, 40·0, 46·05, 50·0, 53·0, 55·0 c.c., respectively, of sodium hydroxide had been added. The following example is typical of the method of calculating these values, except the first and the last, which indicate completion of the different stages of the neutralisation; in these two cases the procedure had to be modified. Point denoting 46·05 c.c. of 0·090*N*-NaOH and *E.M.F.* 0·666 volt. Therefore $[H^{\cdot}] = 10^{-6 \cdot 637}$. It is assumed that the degrees of dissociation of $Na_2CrO_4[\rightleftharpoons 2Na^{\cdot} + CrO_4'']$ and $NaHCrO_4[\rightleftharpoons Na^{\cdot} + HCrO_4']$ are equal (α), and that the relative amount of dissociation of $HCrO_4'$ is negligibly small.

Mols. present in 146 c.c. : $NaOH = 0{\cdot}00414$; $H_2CrO_4 = 0{\cdot}00248$; $Na_2CrO_4 = 0{\cdot}00414 - 0{\cdot}00248 = 0{\cdot}00166$; and $NaHCrO_4 = 0{\cdot}00248 - 0{\cdot}00116 = 0{\cdot}00082$.

Therefore $$K_2 = \frac{[H^{\cdot}][CrO_4'']}{[HCrO_4']} = \frac{[10^{-6{\cdot}637}][\alpha \times (1000/146) \times 0{\cdot}00166]}{[\alpha \times (1000/146) \times 0{\cdot}00082]} = 4{\cdot}67 \times 10^{-7}.$$

It might be supposed, *a priori*, that these two stages of ionisation refer equally well to the dissociation of dichromic acid, $H_2Cr_2O_7$. If this were so, then the salts formed by the neutralisation of the first and of both hydrogen atoms would be $NaHCr_2O_7$ and $Na_2Cr_2O_7$, respectively. The experimental data show, however, that the salts formed contain sodium and chromium in the atomic ratios of 1 : 1 and 2 : 1 and therefore correspond with the formulæ $NaHCrO_4$ and Na_2CrO_4.

2. *Titrations with the Oxygen Electrode.*—Titrations of solutions of chromic acid and sodium hydroxide of concentrations equal to those used in the hydrogen electrode titrations were performed with two oxygen electrodes. These electrodes, freshly platinised, were again of the Hildebrand type, except that one electrode had a loop of platinum wire instead of foil. The chromic acid solution was connected through a bridge of saturated potassium chloride solution with a normal calomel half-element, and the difference in potential between it and each of the oxygen electrodes was measured potentiometrically. The *E.M.F.'s* obtained when the oxygen was passed through the electrode vessel at a fairly quick but uniform rate—about five bubbles per second—were steadier than those measured when the flow of gas was intermittent for the purpose of making readings. When the *E.M.F.* was approximately stationary, the titration was proceeded with as in the hydrogen electrode titration. These initial voltages were far from being equal (see Table II), even after the lapse of 1½ hours.

Curves 1 and 4 in Fig. 2 show the course of this titration as given by these two electrodes.

As the initial *E.M.F.'s* were very different after the electrode had been saturated with oxygen for 1½ hours, an experiment was made to ascertain if identical values could be obtained by prolonging the period of saturation. Five electrodes, two of foil and three of wire, were allowed to remain in 100 c.c. of 0·02475*M*-H_2CrO_4 for 4 days. They were saturated with oxygen for several hours each day. Such treatment was, however, ineffective, for at the end of that time they gave widely different values. Furthermore, the values indicated by the two electrodes which were used

TABLE II.

Showing the variation with time of the initial *E.M.F.'s* in 0·02475*M*-H_2CrO_4 at 18° of oxygen electrodes, measured against the *N*-calomel electrode. The values are referred to the potential difference between the hydrogen electrode in a solution of equal concentration and the *N*-calomel electrode, *i.e.*, they represent the potential difference of an oxygen–hydrogen combination in that particular solution.

Titration.	*E.M.F.* (volts). Foil electrode.	Time.	*E.M.F.* (volts). Loop electrode.	Time.
1	1·159	7 mins.	0·955	7 mins.
	1·162	1½ hrs.	1·039	50 ,,
			1·039	1½ hrs.
2	1·101	5 mins.	1·015	5 mins.
	1·103	4 days	1·045	3 hrs.
			1·080	4 days

in the first titration were appreciably different from those which had previously been found. This will be seen from Tables II and III. Afterwards, the titration of the chromic acid solution with 0·090*N*-sodium hydroxide was followed with each of the five electrodes. The five curves tended to become closer to one another towards the end of the titration. Curves 2 and 3 in Fig. 2 show the results obtained with the two electrodes which had given the respective curves 1 and 4 in the previous titration. The end-points of the two stages of neutralisation are well defined, and for this reason the oxygen electrode is of great service in analytical chemistry, as was pointed out by Furman. The four curves in Fig. 2 are not quite "parallel." By comparing them with the standard curve (Fig. 1), it will be seen that there is a marked tendency for the curves in Fig. 2 to become somewhat elongated in the alkaline zone of the diagram. In other words, the differences between the *E.M.F.'s* of the oxygen and the hydrogen electrodes, each compared with the *N*-calomel electrode for the same solutions, do not remain constant throughout the titration. These differences become smaller and smaller, especially for the alkaline solutions. This will be seen more clearly from Table III, which gives these differences at the beginning, middle (*i.e.*, after the addition of 40 c.c. of sodium hydroxide), and end of the two titrations.

TABLE III.

Electrode.	Foil.		Wire loop.		Wire spiral.	Wire loop.	Foil.
Titration	1	2	1	2	2	2	2
Beginning	1·162	1·103	1·080	1·039	1·070	0·988	1·100
Middle	1·066	1·047	1·013	1·055	1·057	1·022	1·042
End	1·023	0·992	0·965	0·940	0·959	0·960	0·995

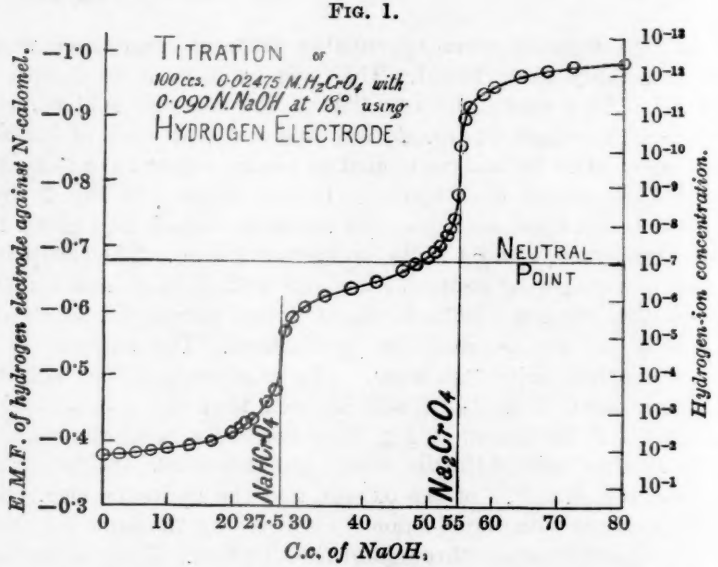
These differences are, as those in Table II, equal to the extrapolated *E.M.F.'s*, the solutions being those at different stages of the titration.

Any scale based upon the assumption that such differences remain constant will therefore be very far from the truth. The scale affixed to Fig. 2 for curve 1 was calculated from the hydrion concentrations of solutions at the beginning and end of the titration. These data were obtained from Fig. 1. This scale, it will be observed by comparison with Fig. 1, gives a fairly accurate measure of the hydrion concentrations throughout the entire titration.

Discussion.

The dissociation of chromic acid in two stages, the second of which corresponds with that of an extremely weak acid, accounts

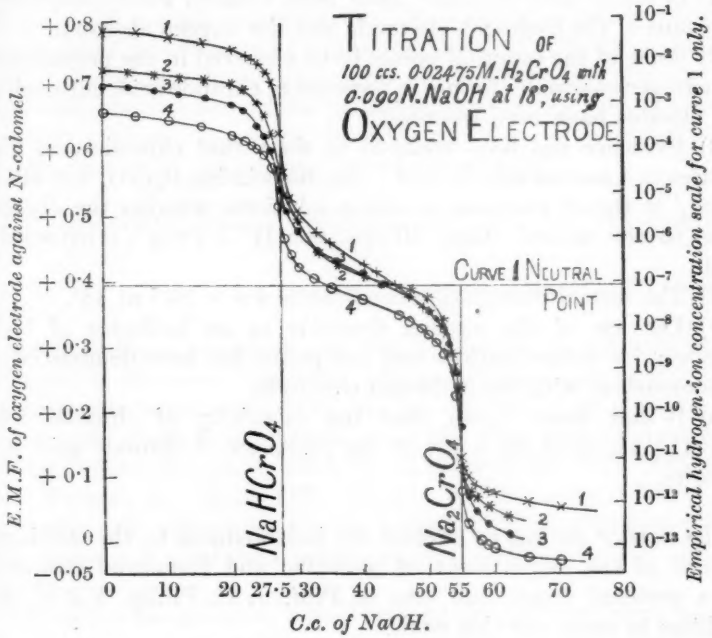
FIG. 1.



for many of the properties of chromates. The addition of alkali chromates to solutions of many metallic salts causes the precipitation of basic salts—a reaction which is peculiar to precipitants the acid radical of which is that of a very weak acid. Many difficultly soluble chromates, *e.g.*, those of silver, the alkaline earths, and the rare earths, dissolve readily in chromic acid. The addition of chromic acid suppresses the concentration of chromate-ions below that required to exceed the solubility product, and this is due to the high concentration of common ions—hydrogen-ions—present in chromic acid solutions, which prevents almost entirely

the further dissociation of the $HCrO_4'$-ions. Reference may also be made to the titration of chromic acid with sodium hydroxide and phenolphthalein. Bruhns (*J. pr. Chem.*, 1916, [ii], **93**, 95, 312) and later Kolthoff and Vogelenzang (*Rec. trav. chim.*, 1921, **40**, 681) observed that the pink colour of phenolphthalein often appears before the whole of the alkali required for complete neutralisation has been added. It will be seen from Fig. 1 that the neutralisation is not quite complete when the hydrion concentration $10^{-8.2}$, at which the indicator begins to change colour, is reached,

FIG. 2.



and, moreover, for some time before this concentration is reached the hydrogen-ion concentration is not much greater than that required to colour the phenolphthalein. This would explain the slow disappearance of the pink colour before the end-point is actually reached. There seems to be no need to postulate, as did the latter workers, that the slowness is due to the time required either for the hydration of Cr_2O_7'' to form $HCrO_4'$, or for the union of Cr_2O_7'' with OH' to form CrO_4'' and water.

Finally, some reference should be made to the characteristic colour changes which occur during the neutralisation of chromic acid. If the colour of the chromate-ion is yellow, then there is

no reason why dichromate and chromic acid solutions also should be yellow, for, as the foregoing experiments show, the concentration of the chromate-ions in such solutions is negligibly small and cannot possibly have any effect on the colour of these solutions. The colour of dichromate solutions must be due largely to the $HCrO_4'$-ions, and the somewhat darker red shade of free chromic acid solutions must be produced by both $HCrO_4'$-ions and either molecules or hydrated aggregates of chromic acid.

Summary.

(1) Chromic acid solutions have been titrated electrometrically by means of the hydrogen electrode and the oxygen electrode.

(2) Some of the essential points to be observed in the preparation of hydrogen electrodes for use in presence of chromic acid, chromates, and nitrates have been recorded.

(3) Evidence has been adduced to show that chromic acid dissociates as a normal dibasic acid. The dissociation $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4'$ is almost complete in dilute solutions, whereas the dissociation to the second stage, $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$, is extremely small.

(4) The second dissociation constant is $4{\cdot}4 \times 10^{-7}$ at 18°.

(5) The use of the oxygen electrode as an indicator of both hydrogen-ion concentrations and end-points has been demonstrated by comparison with the hydrogen electrode.

(6) It has been shown that the dibasicity of chromic acid (H_2CrO_4) accounts for some of the reactions of chromic acid and its salts.

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CCVIII.—*Catalytic Racemisation of the Diastereoisomeric* l-*Menthyl Phenylbromoacetates.*

By ALEX. MCKENZIE and ISOBEL AGNES SMITH.

IN the course of a previous research (J., 1923, **123**, 1962) a description was given of the hydrolysis of the *l*-menthyl phenylchloroacetates. It was then shown that the menthyl ester of the *l*-chloro-

acid gave an acid with the slight lævorotation of $[\alpha]_D$ −1·6° in ethyl-alcoholic solution, the hydrolysis having been conducted under mild conditions with a slight excess of alcoholic potash. When the high optical rotatory power of *l*-phenylchloroacetic acid, namely $[\alpha]_D$ −155·8° in the same solvent, is recalled, the magnitude of the racemisation induced by the alcoholic alkali is at once obvious. On the other hand, when the menthyl ester of the *d*-chloro-acid was submitted to a similar treatment, the result was unexpected, because the acid obtained from the hydrolysis was not dextro- but was lævo-, giving $[\alpha]_D$ −1·3° in ethyl-alcoholic solution. Since the dextro-ester thus resembled its lævo-isomeride in giving on hydrolysis an acid with a slight lævorotation, the deduction was drawn that the complete hydrolysis of *l*-menthyl *dl*-phenylchloroacetate should lead to the formation, not of an optically inactive, but of a slightly lævo-acid, and the correctness of this deduction was proved experimentally. Thus, *r*-phenylchloroacetic acid can be activated very slightly, but quite definitely, through the stages :

$$r\text{-}C_6H_5\cdot CHCl\cdot CO_2H \longrightarrow \underset{(dl\text{-})}{C_6H_5\cdot CHCl\cdot CO_2\cdot} \underset{(l\text{-})}{C_{10}H_{19}} \longrightarrow (\text{by complete hydrolysis}) \; r\text{-} + l\text{-}C_6H_5\cdot CHCl\cdot CO_2H.$$

Owing to the greater ease with which bromine, as compared with chlorine, is displaced by other groups, *l*-phenylchloroacetic and *l*-phenylbromoacetic acids exhibited some points of difference when they were studied in connexion with the Walden inversion (McKenzie and Clough, J., 1908, **93**, 811; 1909, **95**, 777; McKenzie and Walker, J., 1915, **107**, 1685). We have accordingly investigated the diastereoisomeric *l*-menthyl phenylbromoacetates with respect to catalytic racemisation, and the results are as follows.

The esters in question were obtained by the resolution of the *dl*-ester. The ester of the *d*-acid was isolated with ease; it is sparingly soluble in ethyl alcohol, melts at 78—79°, and has $[\alpha]_D$ + 9·4° (c = 2·7744) in ethyl-alcoholic solution. The ester of the *l*-acid is not so readily accessible in a condition of optical purity; it melts at 40—41°, and has $[\alpha]_D$ − 146·1° (c = 3·7205) in ethyl-alcoholic solution.

Since *l*-menthyl *l*-phenylchloroacetate can be prepared directly from the *l*-chloro-acid by conducting the esterification with hydrogen chloride (McKenzie and Smith, *loc. cit.*), attempts were made to prepare the corresponding bromo-ester by the same method. *l*-Phenylbromoacetic acid, when esterified by *l*-menthol and hydrogen chloride, gave a solid which was crystallised several times from

rectified spirit; the resulting crystals consisted of the ester, not of the *l*-acid, but of the *d*-acid. Catalytic racemisation had obviously occurred during the esterification, the *l*-menthyl *l*-phenylbromoacetate being converted into a mixture of the diastereoisomerides, and the crystallisation of this mixture led to the separation of *l*-menthyl *d*-phenylbromoacetate. The latter ester can also be catalytically racemised; it was heated with alcoholic hydrogen chloride, and the recovered ester was then not dextro- but was lævo-, giving $[\alpha]_D$ — 77·9° (c = 1·6744) in ethyl-alcoholic solution. This product consisted of a mixture of the diastereoisomerides with a slight preponderance of the lævo-ester, and from such a mixture the homogeneous lævo-ester can be separated. By taking advantage of the catalytic racemisation induced by the alcoholic hydrogen chloride at the phenylbromoacetyl portion of the molecule, the following changes can accordingly be realised:

$$l\text{-}C_6H_5\cdot CHBr\cdot CO_2H \longrightarrow$$

$$\left.\begin{matrix} (l\text{-}) \quad\quad (l\text{-}) \\ C_6H_5\cdot CHBr\cdot CO_2\cdot C_{10}H_{19} \\ + \\ C_6H_5\cdot CHBr\cdot CO_2\cdot C_{10}H_{19}\cdot \\ (d\text{-}) \quad\quad (l\text{-}) \end{matrix}\right\} \rightleftarrows \begin{matrix} (l\text{-}) \quad\quad (l\text{-}) \\ C_6H_5\cdot CHBr\cdot CO_2\cdot C_{10}H_{19}\cdot \end{matrix} \quad \begin{matrix} (l\text{-}) \quad\quad (l\text{-}) \\ C_6H_5\cdot CHBr\cdot CO_2\cdot C_{10}H_{19}\cdot \\ (d\text{-}) \quad\quad (l\text{-}) \end{matrix}$$

When sulphuric acid is employed instead of hydrogen chloride in esterifying *l*-phenylbromoacetic acid with *l*-menthol, the menthyl ester of the *l*-acid can be obtained directly, and the catalytic racemisation observed under those conditions was not pronounced.

The complete hydrolysis of *l*-menthyl *d*-phenylbromoacetate with an excess of alcoholic potash gave an acid which generally was feebly lævorotatory, and consisted mainly of mandelic acid owing to the hydroxylation of the phenylbromoacetic acid. Sometimes no optical activity could be detected at all, a result which was by no means surprising in the light of the observations already recorded on the profound racemisation which accompanies the displacement of the bromine in *l*-phenylbromoacetic acid by the hydroxyl group (McKenzie and Walker, *loc. cit.*). The interpretation which was previously advanced by us in connexion with the hydrolysis of *l*-menthyl *d*-phenylchloroacetate may also be applied to the above observation with the dextro-bromo-ester, where, however, the result is not so definite.

The partial hydrolysis of *l*-menthyl *d*-phenylbromoacetate gave an acid which was practically optically inactive, whilst the unhydrolysed ester had $[\alpha]_D$ — 65·5° as compared with $[\alpha]_D$ + 9·4° of the ester prior to the addition of the alcoholic alkali. This very pronounced catalytic racemisation suggested that experiments

should be carried out by the addition of very small quantities of alcoholic alkali to a solution of the dextro-ester; the catalyst might show a marked effect in promoting racemisation before it would disappear owing to its hydrolysing action on the ester. Those experiments were successful. In one instance, for example, where the initial value of the alcoholic solution of the dextro-ester was $\alpha_D + 0{\cdot}28°$, the sign of the rotation quickly swung round under the influence of three drops of alcoholic potash (0·4487 *N*), until after 38 minutes a maximum of $\alpha_D - 1{\cdot}98°$ was reached. The latter figure corresponds approximately with $[\alpha]_D - 68°$, and since the value for *l*-menthyl *dl*-phenylbromoacetate, when calculated from the values for the diastereoisomeric esters, is $[\alpha]_D - 68{\cdot}3°$, it was thus clear that the catalytic racemisation had led to the formation of equal quantities of the diastereoisomeric esters. In an experiment conducted with *l*-menthyl *l*-phenylbromoacetate under conditions comparable with the preceding, the initial lævorotation of $\alpha_D - 4{\cdot}22°$ dropped to $- 2{\cdot}36°$ after 38 minutes, and the latter value corresponds approximately with $[\alpha]_D - 82°$. It will be noticed that, when the results arrived at from the two esters are compared, the same end-point is not reached; with the dextro-ester the diastereoisomerides are present in equal amounts after 38 minutes, whereas with the lævo-ester this is not the case. A difference so great as that observed cannot be explained on the basis of the unequal rates of saponification of the two esters, since this factor is almost negligible with the concentration of alkali which was employed. The interpretation is to be found in the unequal velocities of racemisation, and the following results show that *l*-menthyl *d*-phenylbromoacetate undergoes catalytic racemisation more quickly than its diastereoisomeride (for details, see experimental part).

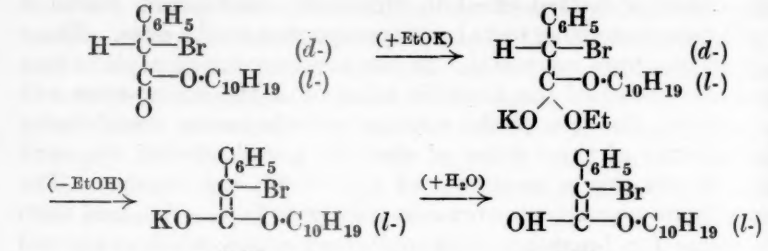
Dextro-ester. a = approximate percentage amount of original ester after catalysis.

Alkali.	Time (mins.).	a.	Alkali.	Time (mins.).	a.
3 drops	10	59	1 drop	20	63
,,	20	52	,,	30	59
1 drop	10	75	,,	40	56

The lævo-ester, when treated similarly, gave the following figures for a: 65, 60; 82, 74, 67, 63.

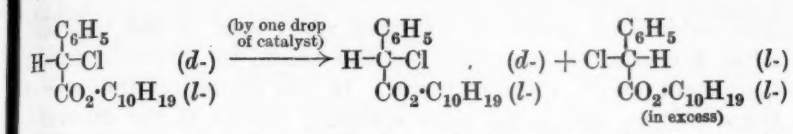
McKenzie and Wren (*inter alia*, J., 1919, **115**, 602) have shown that in the saponification of optically active esters with a migrational hydrogen atom the active agent so far as racemisation is concerned is the metallic alkyloxide. The following scheme

is accordingly now suggested in connexion with *l*-menthyl *d*-phenylbromoacetate :



The addition of potassium ethoxide to form a compound in which the asymmetry of the phenylbromoacetyl complex is retained seems a reasonable supposition, especially in the light of the recent work of Scheibler on ester-enolates and keten-acetals. In the final desmotropic change represented above, where the phenylbromoacetyl complex is regenerated, the asymmetric guiding influence of the *l*-menthyl group might be exerted in such a fashion that one of the diastereoisomerides would preponderate. It is true that in the experiments just described, in which the dextro-ester is catalytically racemised by a trace of ethoxide, an equal amount of the lævo-ester is formed, but this is a result which we consider to be fortuitous. With the lævo-ester the racemisation is not quite so pronounced, and it is highly probable that in this case the catalyst had disappeared before its full effect had been exercised. This point is best brought out by reference to curves, which can be constructed from data recorded in the experimental section.

As it was possible that the catalytic influence of the potassium ethoxide might be even more completely exercised with the corresponding chloro-esters (*loc. cit.*), it was obviously desirable that these should be studied from the same point of view as the analogous bromo-compounds. After addition of a single drop of alcoholic potash (0·4487*N*) to an alcoholic solution of *l*-menthyl *d*-phenylchloroacetate giving α_D + 0·16°, the sign of the rotation changed quickly to lævo-, and after 96 minutes a maximum value of α_D — 2·50° was attained. Since this value corresponds approximately with $[\alpha]_D$ — 86°, and since *l*-menthyl *dl*-phenylchloroacetate has $[\alpha]_D$ — 72·15° (*loc. cit.*), it was thus apparent that the effect of the catalyst was to induce a preponderance of the lævo-ester, and the following result is thus definitely established :



Whilst this action cannot in the orthodox sense of the term be called an asymmetric synthesis, it is an example of *the influence of an optically active group in directing a desmotropic change asymmetrically.*

Again, starting with an alcoholic solution of *l*-menthyl *l*-phenylchloroacetate with α_D — 4·35°, and adding a single drop of the catalyst as before, we observed the value α_D — 2·49° after 2 hours, and this again corresponds approximately with $[\alpha]_D$ — 86°. With the chloro-esters, therefore, the same end-point was apparently reached, and the full effect of the catalyst was brought into action. This point is rendered clearer if the results obtained (more particularly those by the addition of 3 drops of the catalyst to each of the diastereoisomeric esters) are represented by curves.

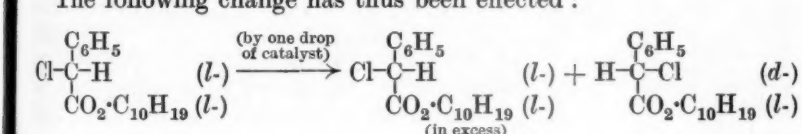
The velocity of the catalysis is greater with *l*-menthyl *d*-phenylchloroacetate than with its diastereoisomeride (for details, see experimental part), thus :

Dextro-ester. a = approximate percentage amount of original ester after catalysis.

Alkali.	Time (mins.).	a.	Alkali.	Time (mins.).	a.
3 drops	10	44	1 drop	30	53
,,	20	43	,,	40	49
1 drop	10	69	,,	2 hours	41
,,	20	58			

The lævo-ester when treated similarly gave the following figures for a: 59, 58; 77, 69, 65, 63, 59.

The following change has thus been effected :



EXPERIMENTAL.

Resolution of l-*Menthyl* dl-*Phenylbromoacetate into its Diastereoisomerides.*—The following is a description of a typical preparation. *r*-Phenylbromoacetic acid (50 gms.) was esterified by heating at about 100° for 9 hours with *l*-menthol (150 gms.) in presence of hydrogen chloride. The ethereal solution was washed with a dilute solution of sodium hydrogen carbonate, the ether and the excess of menthol were then removed, the latter by steam-distillation.

The residual oil gradually solidified when kept in the ice-chest. After 6 crystallisations from rectified spirit, the crystals showed a constant specific rotatory power. In this resolution, the ester of the *d*-halogen acid is the more sparingly soluble of the diastereoisomerides, as is the case also in the resolution of *l*-menthyl *dl*-phenylchloroacetate (*loc. cit.*). Yield = 16 grams.

l-*Menthyl* d-*phenylbromoacetate*, $C_6H_5 \cdot CHBr \cdot CO_2 \cdot C_{10}H_{19}$, m. p. 78—79°, fine needles from ethyl alcohol (Found: Br = 22·7. $C_{18}H_{25}O_2Br$ requires Br = 22·6 per cent.), is readily soluble in acetone, chloroform, light petroleum, benzene, toluene, xylene, trichloroethylene, carbon tetrachloride and ethyl acetate, but somewhat sparingly soluble in ethyl alcohol. Its specific rotation was determined in ethyl-alcoholic solution: $l = 2$, $c = 2{\cdot}7744$, $\alpha_D^{18°} + 0{\cdot}52°$, $[\alpha]_D^{18°} + 9{\cdot}4°$; $\alpha_{5461}^{18°} + 0{\cdot}73°$, $[\alpha]_{5461}^{18°} + 13{\cdot}2°$.

Shimomura and Cohen (J., 1921, **119**, 1816) combined *dl*-phenylbromoacetyl bromide with *l*-menthol and crystallised the product repeatedly from alcohol. They obtained an ester melting at 84° and showing $[\alpha]_D^{19°} + 2{\cdot}2°$ ($c = 0{\cdot}68$, $l = 2$) in alcoholic solution, the suggestion being made that this small dextrorotation is probably due to partial resolution of the acid radical. We have never succeeded in obtaining the melting point of the ester so high as 84°. The polarimetric data given by Shimomura and Cohen are not such as to enable one to judge if the resolution had been carried to a completion; the concentration selected by them is small, the observed angle of rotation when calculated from their figures being $\alpha_D + 0{\cdot}03°$.

l-*Menthyl* l-*phenylbromoacetate*, $C_6H_5 \cdot CHBr \cdot CO_2 \cdot C_{10}H_{19}$, was obtained by prolonged fractional crystallisation of the mother-liquors from the preparation of the *d*-ester. It is readily soluble in ethyl alcohol and crystallises from aqueous ethyl alcohol in fine needles, m. p. 40—41° (Found: C = 61·0; H = 7·3. $C_{18}H_{25}O_2Br$ requires C = 61·2; H = 7·1 per cent.). In ethyl alcohol: $l = 2$, $c = 3{\cdot}7205$, $\alpha_D^{15°} - 10{\cdot}87°$, $[\alpha]_D^{15°} - 146{\cdot}1°$; $\alpha_{5461}^{15°} - 12{\cdot}86°$, $[\alpha]_{5461}^{15°} - 172{\cdot}8°$. In benzene: $l = 2$, $c = 3{\cdot}2835$, $\alpha_D^{17°} - 9{\cdot}18°$, $[\alpha]_D^{17°} - 139{\cdot}8°$; $\alpha_{5461}^{17°} - 10{\cdot}96°$, $[\alpha]_{5461}^{17°} - 166{\cdot}9°$.

Esterification of l-*Phenylbromoacetic Acid with* l-*Menthol.*—(1) *By concentrated sulphuric acid.* *r*-Phenylbromoacetic acid was resolved by morphine (McKenzie and Walker, J., 1915, **107**, 1685). The resulting *l*-acid had $[\alpha]_D^{14°} - 147{\cdot}7°$ for $c = 2{\cdot}03$ in benzene, the value previously quoted being $[\alpha]_D^{13·5°} - 147{\cdot}0°$ ($c = 2{\cdot}0065$). A mixture of *l*-phenylbromoacetic acid (2·8 gms.), *l*-menthol (8·4 gms.), and sulphuric acid (0·84 gm.) was heated on the steam-bath for 6 hours. After the customary manipulation, the ester gave the following value after two crystallisations from rectified spirit. In ethyl

alcohol: $l = 2$, $c = 3{\cdot}394$, $\alpha_D^{14°} - 8{\cdot}91°$, $[\alpha]_D^{14°} - 131{\cdot}3°$ (Found: Br = 22·4. Calc., Br = 22·6 per cent.).

(2) *By hydrogen chloride.* *l*-Phenylbromoacetic acid (3·3 gms.) was heated on the steam-bath for 6 hours with 9·9 gms. of *l*-menthol in presence of hydrogen chloride. The product was manipulated as in the resolution of the *l*-menthyl *dl*-phenylbromoacetate. The resulting solid was crystallised once from rectified spirit and then gave the following values in ethyl alcohol: $l = 2$, $c = 3{\cdot}9768$, $\alpha_D^{15°} - 1{\cdot}83°$, $[\alpha]_D^{15°} - 23{\cdot}0°$. Yield = 2 gms.

From the values of the specific rotatory powers of the diastereoisomeric esters it was thus clear that in the above instance we had to deal with an ester mixture containing an excess of the menthyl ester of the *d*-acid. This mixture should give the pure dextro-ester when crystallised sufficiently often, and this was found to be the case. A specimen of the homogeneous *l*-menthyl *d*-phenylbromoacetate was prepared by crystallising the mixture three times from rectified spirit.

Action of Alcoholic Hydrogen Chloride on l-*Menthyl* d-*Phenylbromoacetate.*—Three grams of *l*-menthyl *d*-phenylbromoacetate were heated on the steam-bath for 30 minutes with 150 c.c. of ethyl-alcoholic hydrogen chloride (1·469*N*). The solvent was removed at the ordinary temperature in a vacuum over sulphuric acid. The ethereal solution of the product was washed with dilute sodium hydrogen carbonate, the ether expelled, and the menthol removed by steam distillation. The residual oil was extracted with ether, and after the removal of the solvent 2 gms. of ester, m. p. 34—50°, were obtained. In ethyl alcohol: $l = 2$, $c = 1{\cdot}6744$, $\alpha_D^{13·5°} - 2{\cdot}61°$, $[\alpha]_D^{13·5°} - 77{\cdot}9°$.

Hydrolysis of l-*Menthyl* d-*Phenylbromoacetate.*—*Complete hydrolysis with excess of alcoholic alkali.* 10·5 C.c. of ethyl-alcoholic potash (0·6849*N*) were added to a solution of 2 gms. of *l*-menthyl *d*-phenylbromoacetate in 25 c.c. of ethyl alcohol, the amount of alkali required for complete hydrolysis being 8·3 c.c. After remaining at the ordinary temperature for 24 hours, the excess of alcohol was removed in a vacuum at the ordinary temperature, water was added, and extraction with ether was carried out eight times in order to ensure the complete removal of the menthol. The aqueous solution was acidified by dilute sulphuric acid, and extracted with ether. The rotation of the resulting acid (0·7 gm.) was taken in benzene: $l = 2$, $c = 4{\cdot}602$, $\alpha_D^{17°} - 0{\cdot}10°$, $[\alpha]_D^{17°} - 1{\cdot}1°$.

In a second experiment the result was similar.

Partial hydrolysis with insufficiency of alcoholic alkali. Six grams of *l*-menthyl *d*-phenylbromoacetate were dissolved by heating with 120 c.c. of ethyl alcohol, and to the cold solution 19 c.c. of ethyl-

alcoholic potash (0·4487*N*) were added, the amount required for complete hydrolysis being 37·9 c.c. After a week at the ordinary temperature, the alcohol was removed as usual, water was added, and the mixture of unhydrolysed ester and menthol was extracted with ether. From this ethereal solution the ester and the menthol were removed, the latter by distillation in steam, and the residual oil was extracted with ether. Two grams of solid ester were obtained and its specific rotation was determined. In ethyl alcohol: $l = 2$, $c = 1{\cdot}6552$, $\alpha_D^{13°} - 2{\cdot}17°$, $[\alpha]_D^{13°} - 65{\cdot}5°$.

This ester on analysis gave Br = 21·2 per cent., and doubtless contained a small admixture of hydroxy-ester or alkyloxy-ester (or both), since the calculated percentage is 22·6. As the distillation of the menthol in steam was carried out for 1½ hours, it is possible that slight displacement of the bromine in the ester by the hydroxyl group may have taken place under those conditions. But in any case the pronounced catalytic racemisation was proved.

The acid which was extracted from the potassium salt obtained from the portion of the ester which was hydrolysed was practically inactive; in benzene solution it gave $\alpha_D - 0{\cdot}03°$ ($c = 2{\cdot}64$).

In another experiment, the catalytic racemisation of the ester was again observed, and the acid which was recovered from the aqueous solution of potassium salt from which the menthol and unhydrolysed ester had been separated showed no optical activity. As was expected, it consisted mainly of mandelic acid, since the percentage of bromine amounted only to 8·6.

Catalytic Racemisation of l-*Menthyl* d-*Phenylbromoacetate*.—An ethyl-alcoholic solution of the ester (0·3613 gm.) was made up to 25 c.c. In a 2-dcm. tube, α_D was + 0·28°, whence $[\alpha]_D$ + 9·7°. Three drops (0·06 c.c.) of ethyl-alcoholic potash (0·4487*N*) were added to the solution in the polarimeter tube, the mixture was shaken quickly, and the rotation then taken at intervals. Owing to the rapidity of the catalytic racemisation, only one observation was taken under α_D in the accompanying table; under *t* are given the times after the addition of the alkali.

t.	α_D.	*t*.	α_D.	*t*.	α_D.	*t*.	α_D.
45 sec.	+0·11°	4 min.	−0·81°	9 min.	−1·48°	31 min.	−1·94°
65 „	−0·08	4½ „	−0·95	10 „	−1·56	40 „	−1·98
2 min.	−0·31	5 „	−1·00	12 „	−1·65	4½ hours	−1·93
2½ „	−0·46	6 „	−1·18	14 „	−1·75	24 „	−1·89
3 „	−0·61	7 „	−1·33	17 „	−1·84		
3½ „	−0·68	8 „	−1·39	20 „	−1·90		

As calculated from the maximum value $\alpha_D - 1{\cdot}98°$ observed after 40 minutes, the value for $[\alpha]_D$ is approximately − 68°. This indicates that one-half of the dextro-ester had been converted into

its lævo-isomeride, since the value for *l*-menthyl *dl*-phenylbromoacetate is — 68·35°.

The effect of adding a single drop (0·02 c.c.) of the alcoholic potash to a solution of the dextro-ester is shown as follows: the initial value before the addition of the alkali was $\alpha_D + 0{\cdot}30°$ ($l = 2$).

t.	α_D.	*t.*	α_D.	*t.*	α_D.	*t.*	α_D.
40 sec.	+0·21°	5 min.	−0·49°	15 min.	−1·17°	1 hour	−1·81°
1½ min.	−0·05	6 ,,	−0·59	18 ,,	−1·35	2 hours	−1·96
2 ,,	−0·11	7 ,,	−0·69	23 ,,	−1·46	5 ,,	−1·97
2½ ,,	−0·21	8 ,,	−0·76	30 ,,	−1·56	3 days	−1·91
3 ,,	−0·31	10 ,,	−0·86	38 ,,	−1·67		
4 ,,	−0·36	12 ,,	−1·01	45 ,,	−1·76		

Calculating from the maximum value observed after 2 hours, $[\alpha]_D$ is again approximately — 68°.

When 3 drops of pyridine were added to a solution of the *d*-ester with $\alpha_D + 0{\cdot}29°$ in a 2-dcm. tube, the rotation rose slightly to + 0·38° after 30 seconds, and then proceeded to fall gradually until, after 6 minutes, the original value was attained. After 17 hours, α_D was + 0·25°. Similarly, a slight initial rise was observed by the addition of 3 drops of alcoholic ammonia to a solution of the *d*-ester with $\alpha_D + 0{\cdot}31°$ in a 2-dcm. tube, the value being + 0·37° 30 seconds after the addition of the ammonia. After 9 minutes the original value was observed, and the solution then proceeded to change its sign very slowly. After 11 days, α_D was − 0·12°. In this case, therefore, the rate of the racemisation was very slow. No catalytic racemisation was observed when 3 drops of alcoholic hydrogen chloride were added to a solution of the *d*-ester with $\alpha_D + 0{\cdot}31°$ in a 2-dcm. tube.

Catalytic Racemisation of l-*Menthyl* l-*Phenylbromoacetate.*

0·3612 Gm. of the ester to 25 c.c. with ethyl alcohol; α_D ($l = 2$) − 4·22°, whence $[\alpha]_D$ — 146°; three drops (0·06 c.c.) of ethyl-alcoholic potash (0·4487*N*).

t.	α_D.	*t.*	α_D.	*t.*	α_D.	*t.*	α_D.
½ min.	−4·06°	3 min.	−3·32°	9 min.	−2·72°	40 min.	−2·36°
1 ,,	−3·86	3½ ,,	−3·27	12 ,,	−2·55	4 hours	−2·23
1½ ,,	−3·70	4 ,,	−3·20	15 ,,	−2·49	23 ,,	−2·09
2 ,,	−3·62	5 ,,	−3·01	24 ,,	−2·40		
2½ ,,	−3·46	6 ,,	−2·89	30 ,,	−2·35		

The value after 40 minutes corresponds with $[\alpha]_D$ of approximately − 82°, whereas the value after 23 hours corresponds with $[\alpha]_D$ of approximately — 72°.

The effect of adding a single drop (0·02 c.c.) of the alcoholic potash to a solution of the lævo-ester is shown as follows; the initial value before the addition of the alkali was $\alpha_D - 4{\cdot}17°$ ($l = 2$).

$t.$	α_D.	$t.$	α_D.	$t.$	α_D.	$t.$	α_D.
1 min.	−4·12°	5 min.	−3·68°	15 min.	−3·15°	1 hour	−2·42°
1½ ,,	−4·00	6 ,,	−3·62	18 ,,	−3·07	2 hours	−2·32
2 ,,	−3·95	7 ,,	−3·56	24 ,,	−2·88	7 ,,	−2·28
2½ ,,	−3·91	8 ,,	−3·51	30 ,,	−2·74	3 days	−2·22
3 ,,	−3·86	10 ,,	−3·40	40 ,,	−2·57		
4 ,,	−3·80	12 ,,	−3·32	45 ,,	−2·48		

Calculating from the value observed after 2 hours, $[\alpha]_D$ is approximately − 80°.

Catalytic Racemisation of l-*Menthyl* d-*Phenylchloroacetate.*

0·361 Gm. of the dextro-ester (*loc. cit.*) to 25 c.c. with ethyl alcohol; α_D + 0·16° ($l = 2$), whence $[\alpha]_D$ + 5·5°; one drop (0·02 c.c.) of ethyl-alcoholic potash (0·4487*N*).

$t.$	α_D.	$t.$	α_D.	$t.$	α_D.	$t.$	α_D.
20 sec.	+0·06°	7 min.	−1·03°	25 min.	−1·85°	96 min.	−2·50°
40 ,,	+0·01	10 ,,	−1·21	30 ,,	−1·97	132 ,,	−2·48
2 min.	−0·25	13 ,,	−1·38	36 ,,	−2·05	18 hours	−2·43
3 ,,	−0·45	16 ,,	−1·55	42 ,,	−2·13		
4 ,,	−0·63	19 ,,	−1·68	50 ,,	−2·28		
5 ,,	−0·79	22 ,,	−1·78	62 ,,	−2·33		

The maximum lævorotation observed was α_D − 2·50°, which corresponds approximately with $[\alpha]_D$ − 86·5°. At this stage, the product was thus a mixture of the diastereoisomeric esters with a preponderance of the lævo-ester, since *l*-menthyl *dl*-phenylchloroacetate (*loc. cit.*) has $[\alpha]_D$ − 72·15°.

The effect of adding 3 drops (0·06 c.c.) of the alcoholic potash to a solution of the dextro-ester with α_D + 0·16° ($l = 2$) is shown thus:

$t.$	α_D.	$t.$	α_D.	$t.$	α_D.	$t.$	α_D.
½ min.	−0·22°	3 min.	−1·73°	8 min.	−2·29°	20 min.	−2·40°
1 ,,	−0·79	4 ,,	−1·91	9 ,,	−2·31	23 ,,	−2·44
1½ ,,	−1·06	5 ,,	−2·06	10 ,,	−2·34	1½ hours	−2·40
2 ,,	−1·34	6 ,,	−2·14	13 ,,	−2·36	3½ days	−2·22
2½ ,,	−1·55	7 ,,	−2·24	15 ,,	−2·38		

Calculating from the maximum value − 2·44°, $[\alpha]_D$ is approximately − 84°.

Catalytic Racemisation of l-*Menthyl* l-*Phenylchloroacetate.*

0·3612 Gm. of the lævo-ester (*loc. cit.*) to 25 c.c. with ethyl alcohol; α_D − 4·35° ($l = 2$), whence $[\alpha]_D$ − 150·5°; one drop (0·02 c.c.) of ethyl-alcoholic potash (0·4487*N*).

$t.$	α_D.	$t.$	α_D.	$t.$	α_D.	$t.$	α_D.
20 sec.	−4·23°	5 min.	−3·68°	16 min.	−3·01°	60 min.	−2·62°
2 min.	−4·03	7 ,,	−3·49	22 ,,	−2·93	80 ,,	−2·58
3 ,,	−3·85	10 ,,	−3·29	30 ,,	−2·78	2 hours	−2·49
4 ,,	−3·77	13 ,,	−3·12	41 ,,	−2·67	18 ,,	−2·47

The value after 2 hours, namely, α_D — 2·49°, corresponds with $[\alpha]_D$ of approximately — 86°.

The effect of adding 3 drops (0·06 c.c.) of the alcoholic potash to a solution of the lævo-ester with α_D — 4·35° ($l = 2$) is shown thus :

t.	α_D.	*t.*	α_D.	*t.*	α_D.	*t.*	α_D.
25 sec.	−4·01°	3 min.	−3·03°	8 min.	−2·57°	48 min.	−2·36°
55 ,,	−3·72	4 ,,	−2·85	9 ,,	−2·53	5¾ hours	−2·27
1½ min.	−3·51	5 ,,	−2·73	10 ,,	−2·49		
2 ,,	−3·27	6 ,,	−2·65	11 ,,	−2·45		
2½ ,,	−3·15	7 ,,	−2·63	13 ,,	−2·43		

Calculating from the value α_D — 2·43° attained after 13 minutes, $[\alpha]_D$ is approximately — 84°.

One of us wishes to express her best thanks to the Carnegie Trust for the award of a Fellowship which enabled this work to be carried out.

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, April 2nd,* 1924.]

CCIX.—*The Rotatory Dispersive Power of Organic Compounds. Part XII. Octyl Alcohol and Octyl Oxalate.*

By THOMAS MARTIN LOWRY and EVAN MATTHEW RICHARDS.

THE fact that the rotatory dispersion of simple optically-active alcohols and acids can be expressed by the "simple" formula $\alpha = k/(\lambda^2 - \lambda_0^2)$ was established in 1913 (J., 1913, **103**, 1074) by means of measurements made with a series of some seven or eight wave-lengths only. Subsequent experience has shown that cases exist in which this formula is obeyed very closely, but that, when a long series of careful measurements is made, small systematic errors are disclosed, which can only be eliminated by using a more complex formula. An example of this kind was discovered (Lowry and Austin, *Phil. Trans.*, 1922, [*A*], **222**, 249) in aqueous solutions of sodium tartrate, which almost exactly obeyed Biot's Law $\alpha = k/\lambda^2$. The "simple" formula, which very nearly expressed the dispersion of this compound, was already under suspicion on account of the extreme smallness of the constant λ_0^2; but confirmation of the inaccuracy of this formula was only obtained when a series of measurements for some 20 wave-lengths revealed a group of small positive errors between the green and violet mercury lines, with negative errors outside these limits, thus proving that the experi-

mental data curved away slightly from the calculated rotations. In another case, of which no account has yet been published, a substance which appeared to obey the " simple " dispersion formula when the rough graphical method was applied to readings for four wave-lengths in the visible region only, gave very large deviations indeed when the dispersion curve was followed into the ultra-violet region; fuller investigation proved that the whole curve was complex in character, but could be represented satisfactorily by a two-term equation of the Drude type.

In these circumstances, it appeared to be desirable to test again, with all the added refinements that have been developed during the past 10 years, the validity of the one-term equation as applied to the optically active secondary alcohols. At the same time it was thought that a careful test, similar to that carried out with ethyl tartrate (Lowry and Cutter, J., 1922, **121**, 532), might serve to establish the validity of the two-term equation in the case of those esters of these alcohols of which the dispersion was known to be complex.

The alcohols selected were *d*- and *l*-octyl alcohol, and the ester was di-*l*-octyl oxalate. These materials were very kindly supplied by Dr. R. H. Pickard. In the case of the alcohol, the *d*- and *l*-isomerides were available in sufficient quantities to fill a pair of 6-dcm. tubes; it was therefore possible, by reading one tube against the other, to double the magnitude of the observed rotations, and at the same time to take both readings under precisely similar conditions, instead of under the altered conditions which are normally encountered when the tube is taken out in order to read the zero. Since the rotations of the two alcohols did not balance exactly, it was assumed that the higher value was correct. In the case of the ester, the quantity was sufficient to fill a 2-dcm. tube only, but the actual rotations were of a magnitude similar to those of the alcohols, on account of the higher rotatory power of the compound.

Readings were taken for some 20 wave-lengths between 6708 and 4358, beyond which limits the visual intensity of the light is too small for direct observations with the eye. Photographic observations were then made, up to a point in the early ultra-violet region where excessively long exposure would have been required to produce a record of the rotation. In all, some thousands of visual readings were taken, since the policy was adopted of repeating the readings until the concordance of several independent groups showed that the error in the average of these groups was probably only a few hundredths of a degree for each line. The photographic readings were less exact, especially when nearing the working limit of trans-

TABLE I.

Specific Rotatory Power of *sec.*-Octyl Alcohol (Methylhexylcarbinol).

Mol. wt. 130·16.

$[\alpha] = 3{\cdot}176/(\lambda^2 - 0{\cdot}0244)$.

$\alpha_{5461} = +57{\cdot}13°$ and $-56{\cdot}40°$.

Line.	[α] obs.	[α] calc.	[α] obs.—[α] calc.
Li 6708	7·46°	7·47°	−0·01°
Cd 6438	8·14	8·14	±
Zn 6362	8·35	8·35	±
Na 5893	9·84	9·85	−0·01
Cu 5782	10·25	10·25	±
Hg 5780	10·25	10·26	−0·01
Cu 5700	10·57	10·57	±
Hg 5461	11·61	11·60	+0·01
Cu 5218	12·82	12·81	+0·01
Ag 5209	12·86	12·85	+0·01
Cu 5153	13·18	13·18	±
Cu 5106	13·44	13·44	±
Cd 5086	13·56	13·56	±
Zn 4811	15·36	15·35	+0·01
Cd 4800	15·43	15·42	+0·01
Zn 4722	16·00	15·99	+0·01
Zn 4680	16·33	16·32	+0·01
Cd 4678	16·34	16·34	±
Hg 4358	19·19	19·19	±
Fe 4271	*20·10*	20·10	±
Fe 4261	*20·25*	20·21	+0·04
Fe 4251	*20·35*	20·32	+0·03
Fe 4046	*22·80*	22·80	±
Fe 3860	*25·44*	25·50	−0·06
Fe 3814	*26·16*	26·23	−0·07

Note.—The actual reading of the difference between the two alcohols for Hg 5461 was 113·53°. The factor for reducing the readings to specific rotations was 0·1022 for the visual and 0·2057 for the photographic readings. Values determined by the photographic method are shown in italics.

mission in the ultra-violet; but in the case of several of the lines, the extinction was bracketed by taking photographs at intervals of only 0·2°, and for the majority of the lines the error of reading is probably only a few tenths of a degree.

The results are set out in Tables I and II. They show that octyl alcohol obeys the "simple" dispersion law right up to the limits of experimental error, and over the whole range of wave-lengths used. Octyl oxalate, on the other hand, very nearly obeys Biot's law; but, just as in the case of sodium tartrate, when a long series of careful observations was made, systematic errors were found which showed that the formula is not correct. Thus in the red, yellow, and green regions the errors are all negative, in the blue and violet regions from wave-length 4811 to 4326 they are distributed evenly between positive and negative, whilst in the deep violet and ultra-violet regions they are negative and increasing rapidly.

TABLE II.

Specific Rotatory Power of Di-*l*-Octyl Oxalate. Mol. wt. 314·31.

$$\text{Biot's equation } [\alpha] = \frac{7{\cdot}855}{\lambda^2}.$$

$$\text{Two-term equation } [\alpha] = \frac{10{\cdot}5}{\lambda^2 - 0{\cdot}0244} - \frac{2{\cdot}87}{\lambda^2 - 0{\cdot}06}.$$

		Biot's equation.		Two-term equation.	
Line.	[α] obs.	[α] calc.	[α] obs.— [α] calc.	[α] calc.	[α] obs.— [α] calc.
Li 6708	17·39°	17·46°	−0·07°	17·31°	+0·08°
Cd 6438	18·85	18·95	−0·10	18·82	+0·03
Zn 6362	19·29	19·40	−0·11	19·28	+0·01
Na 5893	22·60	22·63	−0·03	22·54	+0·06
Cu 5782	23·43	23·49	−0·06	23·42	+0·01
Hg 5780	23·43	23·51	−0·08	23·43	±
Cu 5700	24·12	24·17	−0·05	24·11	+0·01
Hg 5461	26·34	26·34	±	26·30	+0·04
Cu 5218	28·82	28·85	−0·03	28·84	−0·02
Ag 5209	28·93	28·95	−0·02	28·94	−0·01
Cu 5153	29·57	29·58	−0·01	29·57	±
Cu 5106	30·06	30·13	−0·07	30·14	−0·08
Cd 5086	30·37	30·37	±	30·37	±
Zn 4811	33·91	33·94	−0·03	33·98	−0·07
Cd 4800	34·17	34·09	+0·08	34·13	+0·04
Zn 4722	35·17	35·22	−0·05	35·26	−0·09
Zn 4680	35·89	35·86	+0·03	35·90	−0·01
Cd 4678	35·91	35·89	+0·02	35·93	−0·02
Fe 4384	*40·97*	40·87	+0·10	40·87	+0·10
Hg 4358	41·29	41·35	−0·06	41·34	−0·05
Fe 4326	*42·01*	41·97	+0·04	41·95	+0·06
Fe 4271	*43·04*	43·06	−0·02	43·01	+0·03
Fe 4228	*43·92*	43·94	−0·02	43·86	+0·06
Fe 4144	*45·60*	45·74	−0·14	45·58	+0·02
Fe 4072	*47·13*	47·37	−0·24	47·13	±
Fe 4046	*47·67*	47·98	−0·31	47·70	−0·03
Fe 4005	*48·49*	48·97	−0·48	48·62	−0·13

Note.—The actual reading for Hg 5461 was −48·34°. The factor for reduction to specific rotations was 0·5448 both for the visible and for the photographic readings. Values determined by the photographic method are shown in italics.

A two-term equation can be devised to express the rotatory power of octyl oxalate for different wave-lengths, but, on account of the smallness of the deviations from Biot's law, it is impossible to determine accurately all the four constants of this equation. Arbitrary values were therefore taken for the two dispersion constants of the ester, one of them being identical with the dispersion constant in the one-term equation for the alcohol, whilst the other served to express the deviations from this equation. Definite values could then be calculated for the two rotation constants; but the resulting equation is put forward only to show that an equation of this type will fit the readings, and not as establishing the correct

values of the four constants. The errors of observation are of the same order of magnitude as in the case of the alcohol, but the divisor used to reduce the readings to specific rotations was smaller (about 2 instead of 10 or 5). Even so, however, the average difference between the observed and calculated rotations for 27 wave-lengths (including eight photographic readings) is only 0·04° and there is only one case in which it is greater than 0·1°.

Summary.

(*a*) The rotatory dispersion of octyl alcohol has been measured with the greatest care for 19 wave-lengths by the visual method and for 6 further wave-lengths by the photographic method. The results can be expressed completely by one term of Drude's equation.

(*b*) The rotatory dispersion of octyl oxalate has been measured for 19 wave-lengths by the visual method and for 8 wave-lengths by the photographic method. As in the case of sodium tartrate, the results approximate closely to the inverse-square law of Biot, but cannot be expressed either by that law or by one term of Drude's equation; the dispersion is therefore not simple but complex.

We are indebted to the Department of Scientific and Industrial Research for financial assistance with the help of which this research was carried out.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, January 7th*, 1924.]

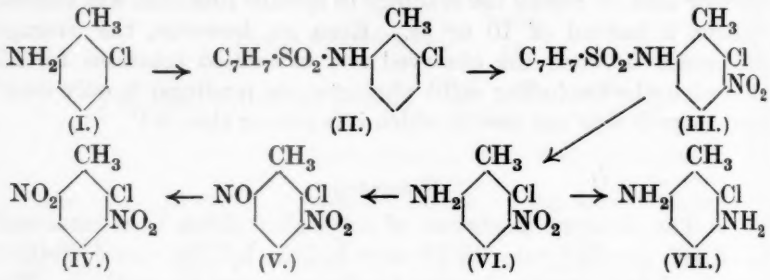
CCX.—ortho-*Chlorodinitrotoluenes. Part V.* 2-*Chloro*-3 : 6-*dinitrotoluene.*

By GILBERT T. MORGAN and THOMAS GLOVER.

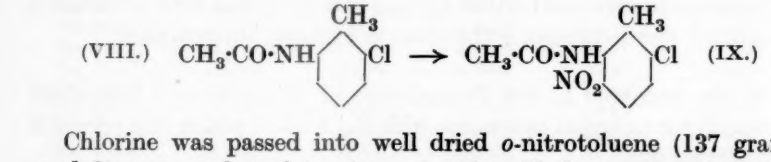
THIS investigation of the chlorodinitrotoluenes was undertaken originally in order to compare the nitration of *o*-chlorotoluene with that of chlorobenzene, the products of the latter operation being substances of considerable technical interest. In earlier researches on this subject by one of us (G.T.M.) and H. D. K. Drew the number of *o*-chlorodinitrotoluenes obtainable by direct nitration of *o*-chlorotoluene or its mononitro-compounds was increased from two to four (J., 1920, **117**, 784) and a fifth isomeride was obtained by an indirect method (J., 1921, **119**, 1700).

The synthesis outlined below leads to 2-chloro-3 : 6-dinitrotoluene

(m. p. 62—63°), thus completing the set of six 2-chlorodinitrotoluenes demanded by theory.



The introduction of a nitro-group into the required ortho-position with respect to chlorine (II and III in the foregoing diagram) depends on the use of a strongly directive substituent such as the toluene-*p*-sulphonyl radical, for when 6-chloroaceto-*o*-toluidide (VIII) is nitrated the main product is 6-*chloro*-3-*nitroaceto*-o-*toluidide* (IX), identified by hydrolysis to 6-*chloro*-3-*nitro*-o-*toluidine* (m. p. 151°).



Chlorine was passed into well dried *o*-nitrotoluene (137 grams) and 20 grams of steel turnings at 40° until the increase in weight was 38 grams. The oily product was left for 12 hours, filtered from iron sludge, and distilled under reduced pressure (150 mm.) to separate the organic material from ferric chloride. The distillate was fractionated under atmospheric pressure and the fraction boiling at 237—241° was cooled at 0° for several days, when 2-chloro-6-nitrotoluene separated in acicular form melting at 35°. The yield by this process was never more than 30 per cent. of the calculated amount. The greater part of the chlorination product remained as an oil. Sixty grams of 2-chloro-6-nitrotoluene were added with shaking during 2 hours to 15 c.c. of crude hydrochloric acid (*d* 1·19) and 150 c.c. of water containing 60 grams of iron filings. After 6 hours, 20 grams of sodium hydroxide were added and 6-chloro-*o*-toluidine (I) was separated by distillation in steam, and extracted from the distillate with ether. The oily base (45 grams) was dried at its boiling point and then treated with 55 grams of toluene-*p*-sulphonyl chloride, the solidified mixture being heated on the water-bath for 1 hour. Saturated aqueous sodium bicarbonate (300 c.c.) was now added, the temperature being maintained at 100° for 1 hour, and the viscid oil, which solidified on cooling, was

purified by crystallising from glacial acetic acid and from alcohol (67 grams).

Toluene-p-*sulphonyl*-6-*chloro*-o-*toluidide* (II), $C_7H_7 \cdot SO_2 \cdot NH \cdot C_7H_6Cl$, crystallised in large, colourless prisms, m. p. 119°; it was readily soluble in cold ether, acetone, or chloroform and moderately soluble in cold benzene or alcohol, dissolving only sparingly in light petroleum (Found : N = 4·93. $C_{14}H_{14}O_2NClS$ requires N = 4·74 per cent.).

Toluene-p-*sulphonyl*-6-*chloro*-5-*nitro*-o-*toluidide* (III),

$$C_7H_7 \cdot SO_2 \cdot NH \cdot C_7H_5Cl \cdot NO_2,$$

was produced by adding 20 grams of the preceding toluidide to 14 c.c. of nitric acid (*d* 1·42) diluted with 100 c.c. of water, the mixture being heated and shaken on the water-bath for 12 hours. At first, the toluidide melted to a heavy, brown syrup evolving bubbles of gas, then gradually the product rose to the surface of the dilute acid as a brown crust, which was thrice crystallised from absolute alcohol; the yield was 12 grams (Found : N = 8·08. $C_{14}H_{13}O_4N_2ClS$ requires N = 8·22 per cent.).

This nitro-compound was moderately soluble in the ordinary organic media with the exception of light petroleum; it separated in well-defined, colourless needles, m. p. 157°.

6-*Chloro*-5-*nitro*-o-*toluidine* (VI).—A solution of the preceding toluene-*p*-sulphonyl derivative (18 grams) in 20 c.c. of cold concentrated sulphuric acid was heated on the water-bath for 10 to 15 minutes; the colour changed from light to dark brown and on adding the solution to 160 grams of chopped ice a mixture of free amine and sulphate separated. After treatment with excess of aqueous sodium hydroxide the crude base was crystallised repeatedly from alcohol, when 3·5 grams were obtained of brown, prismatic needles, m. p. 162° (Found : N = 15·17. $C_7H_7O_2N_2Cl$ requires N = 15·02 per cent.).

This nitroamine was readily soluble in acetone and moderately soluble in alcohol, benzene, or ether, sparingly soluble in chloroform or light petroleum; it dissolved in cold concentrated sulphuric acid or in hot concentrated hydrochloric acid. Its sulphate and hydrochloride were both hydrolysed by excess of water. A mixture of 6-chloro-5-nitro-*o*-toluidine with the isomeric 6-chloro-3-nitro-o-toluidine (m. p. 151°) melted at 120—130°.

2-*Chloro*-3 : 6-*dinitrotoluene* (IV).—To a solution of Caro's acid prepared by mixing 8·5 grams of powdered ammonium persulphate with 6·3 c.c. of concentrated sulphuric acid and after 1 hour pouring the mixture on to 17 grams of crushed ice, were added slowly 1·7 grams of 6-chloro-5-nitro-*o*-toluidine dissolved in 5·2 c.c. of concentrated sulphuric acid. A yellowish-grey solid began to separate

almost at once, but was left for 4 days in contact with the oxidising solution. An equal bulk of water was then added and the 2-*chloro*-6-*nitroso*-3-*nitrotoluene* (V) was collected and introduced in small quantities into 12 c.c. of nitric acid (*d* 1·5), heated on the water-bath. When nitrous fumes were no longer evolved, the pale yellow solution was diluted and cooled, when 2-*chloro*-3 : 6-*dinitrotoluene* separated as a pale yellow oil which soon solidified. After crystallisation from alcohol this product melted at 61° and retained a trace of yellow impurity, but after dissolving in light petroleum (b. p. 40—80°) the colouring matter separated with the first crop of crystals, leaving an almost colourless solution from which 2-*chloro*-3 : 6-*dinitrotoluene* separated in long, brittle, colourless needles, m. p. 61·5—63°, the yield of purified substance being 60 per cent. (Found : N = 13·20; Cl = 16·20. $C_7H_5O_4N_2Cl$ requires N = 12·93; Cl = 16·37 per cent.).

Mixtures of 2-chloro-3 : 6-dinitrotoluene with the 4 : 6-dinitro-isomeride (m. p. 49°) and the 5 : 6-dinitro-isomeride (m. p. 106·5°) melted below laboratory temperature and at 45—80°, respectively.

2-Chloro-3 : 6-dinitrotoluene was very soluble in the usual organic solvents, especially on warming. With alcoholic soda, it gave a transparent, yellow solution which on warming became orange-yellow and finally orange-red. In these colour changes the new dinitro-compound resembled most closely 2-chloro-5 : 6-dinitrotoluene. Liquid ammonia at −70° dissolved it to a light blue solution, which assumed an opaque, brownish-red colour as the temperature rose to the normal. These colour changes did not at first denote any chemical reaction, because on opening the sealed tube and allowing the ammonia to evaporate the unaltered dinitro-compound was recovered. When, however, the sealed tube was left at the ordinary temperature for 3 days the residue on evaporation was a brown solid which would neither crystallise nor melt below 260°. With alcoholic ammonia the 3 : 6-dinitro-compound dissolved to a transparent yellow solution becoming cherry-red, and in sealed tubes at 130° this reagent gave a basic substance crystallising from dilute alcohol in yellow needles, melting at 116—118°, mixed with a small quantity of orange-red amorphous material (Found : N = 17·89; Cl = 14·45. A chloronitrotoluidine requires N = 15·02; Cl = 19·03 per cent.).

When heated with alcoholic aniline for 15 hours under reflux, 2-chloro-3 : 6-dinitrotoluene remained unchanged.

6-*Chloro*-2 : 5-*tolylenediamine* (VII).—Zinc dust (0·6 gram) was slowly added to 1 gram of 6-chloro-5-nitro-*o*-toluidine dissolved in 14 c.c. of alcohol and 5 c.c. of water containing 0·5 gram of ammonium chloride. The mixture was heated under reflux for an hour and

two further quantities of 0·6 gram of zinc dust were added over a period of 2 hours. The solution was filtered while hot and the filtrate cooled in a freezing mixture and saturated with hydrogen chloride, when 0·9 gram of the diamine hydrochloride separated. The base set free by sodium hydroxide was crystallised from petroleum (b. p. 60—80°); it separated in colourless needles, m. p. 89—90° (Found: N = 18·25. $C_7H_9N_2Cl$ requires N = 17·89 per cent.).

6-Chloro-2 : 5-tolylenediamine was very soluble in alcohol and was readily oxidisable in alcoholic solution, although quite stable as a dry solid. Oxidation with acidified potassium dichromate led to the formation of a volatile quinone.

Nitration of 6-Chloroaceto-o-toluidide.—6-Chloroaceto-*o*-toluidide (3 grams) was nitrated either by adding it in small quantities to 15 c.c. of nitric acid (*d* 1·5), cooled in ice, or by pouring the acid on to 2 grams of the toluidide. The nitration product was boiled with 30 c.c. of benzene; the main portion remained undissolved and when crystallised from alcohol melted at 186° (Found: N = 12·33. $C_9H_9O_3N_2Cl$ requires N = 12·25 per cent.).

Nitration performed with concentrated sulphuric acid and potassium nitrate led to a mixture of nitro-compounds, which on hydrolysis furnished 6-chloro-3-nitro-*o*-toluidine (m. p. 151°), this base being the only hydrolytic product identified from the foregoing nitrations of 6-chloroaceto-*o*-toluidide.

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CCXI.—cyclo*Telluropentanediones and* cyclo*Telluripentanedione Dihalides.*

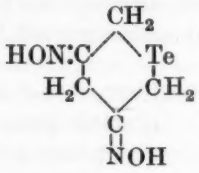
By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

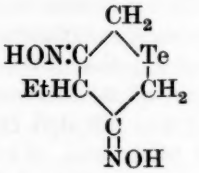
THE interaction of tellurium tetrachloride and 3 : 3-diethylacetylacetone leads to tellurium 3 : 3-diethylacetylacetone dichloride and tellurium 3 : 3-diethylacetylacetone (this vol., p. 735), a result which necessitates a reconsideration of the general constitution ascribed to cyclic tellurium derivatives containing bivalent β-diketonic radicals (*loc. cit.*). A similar condensation occurs even more readily with 3 : 3-dimethylacetylacetone, the simplest β-diketone of the type $RCH_2{\cdot}CO{\cdot}CR'_2{\cdot}CO{\cdot}CH_2R$, and it thus becomes evident that enolisation of the diketone by migration of hydrogen from the median carbon atom is not an essential phase in the production of these cyclic tellurium compounds.

In the present investigation, a representative set of tellurium

β-diketones has been tested with hydroxylamine and the results indicate decisively that these substances are actually diketonic in structure, since they give rise to dioximes. This oximation proceeds in two stages, as is shown by the isolation of mono-oximes.

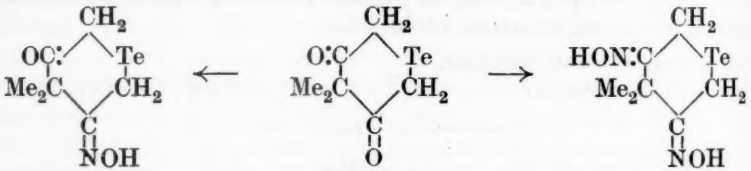
Tellurium acetylacetone (*cyclo*telluropentane-3 : 5-dione) readily yields the *dioxime* (I, cyclo*telluropentane*-3 : 5-*dionedioxime*) and the 3-alkyl derivatives behave similarly, as exemplified by the formation of *tellurium*-3-*ethylacetylacetone dioxime* (II, cyclo*telluro*-4-*ethylpentane*-3 : 5-*dionedioxime*).

(I.) 

 (II.)

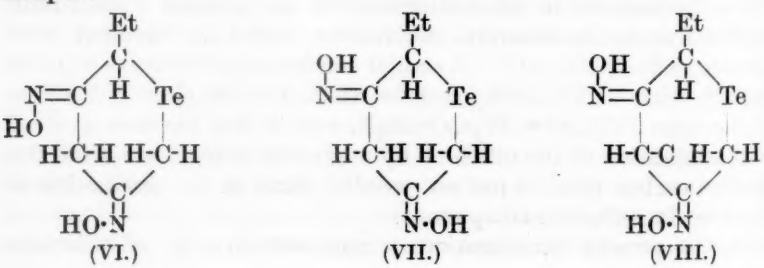
Steric hindrance is apparent as substitution proceeds, and tellurium 3-methylpropionylacetone furnishes its *monoxime* (XV) on oximation in dilute acetic acid and its *dioxime* (XVI) on more drastic treatment in alkaline solution.

Tellurium 3 : 3-*dimethylacetylacetone* (IV) also yields a *monoxime* (III) and a *dioxime* (V) isomeric respectively with the two foregoing compounds.



(III.) (IV.) (V.)

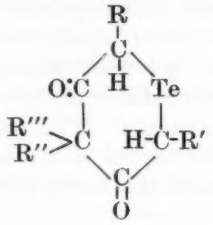
Isomerism of the Hantzsch-Werner type has been observed in the case of the dioximes from tellurium *n*-butyrylacetone. The following formulæ indicate that four modifications are possible:—*syn* (VI), *anti* (VII), and two *amphi* forms (only one shown, VIII), each of which should be resolvable into optically active enantiomorphs.

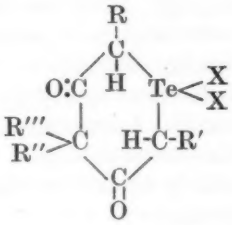


(VI.) (VII.) (VIII.)

Actually, two dioximes have been isolated and designated provisionally as *α-dioxime* (m. p. 149°) and *β-dioxime* (m. p. 183°), which may have respectively the *syn-* and *anti*-configurations.

The fact which emerges definitely from the results recorded below is that the yellow cyclic tellurium β-diketones (IX) of high germicidal power and their corresponding dihalides (X) contain a six-membered ring consisting of five carbon atoms and one tellurium atom united so that the two ketonic carbon atoms are in meta-positions with respect to tellurium.

(IX.) 

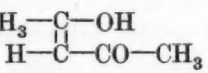
(X.) 

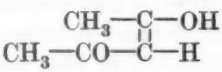
In the foregoing formulæ, X may be Cl, Br, or I, and the symbols R, R′, R″, and R‴ may represent hydrogen atoms or similar or dissimilar alkyl or arylalkyl (*e.g.* benzyl) groups. But one important reservation should be made in the light of many unsuccessful experiments, namely, that these symbols R . . . R‴ do not represent phenyl or other purely aromatic groups. Moreover, the remaining hydrogens attached to the carbon atoms adjacent to tellurium have not been replaced by alkyl groups. The two series may therefore be regarded respectively as cyclo*telluropentane*-3 : 5-*diones* and cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dihalides*, representing two new types of cyclic organometalloidal compounds.

Tautomeric Change among the β-Diketones.

The interactions of acetylacetone and its homologues with (1) metallic compounds, (2) selenium tetrachloride, and (3) tellurium tetrachloride reveal the existence of three dynamic isomerides of these diketones.

1. In the production of metallic β-diketones, such as copper acetylacetone, the diketone reacts in the *trans*-monoenolic form (XI); the metallic radical replacing hydroxylic hydrogen co-

(XI.) 

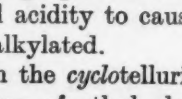
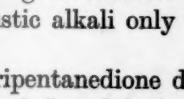
 (XII.)

ordinates with the adjacent carbonyl oxygen, thus completing the six-membered ring. This mode of condensation also occurs in the β-diketonic derivatives of boron, silicon, germanium, titanium, tin, and zirconium (*Annalen*, 1905, **344**, 326; this vol., p. 372).

2. The *cis*-monoenolic form (XII) is operative in the condensation with selenium tetrachloride. The two reactive hydrogen atoms of the hydroxyl group and the CH- residue are now contiguous and are both replaced by selenium with the formation of two five-membered rings having two selenium atoms in common (J., 1922, **121**, 2435).

3. Condensation with tellurium tetrachloride reveals a diketonic modification of acetylacetone when the metalloid replaces one hydrogen from each of the methyl groups and completes the six-membered ring. With the establishment of this closed system, enolisation is no longer possible except under conditions of considerable strain tending to disrupt the *cyclo*telluropentane ring. This stereochemical conception of tellurium β-diketones is supported by the chemical behaviour of these substances; they are devoid of enolic properties in regard to ferric and copper salts; and show residual acidity to caustic alkali only when the methylene radical is non-alkylated.

When the *cyclo*telluripentanedione dichlorides are transformed, by means of ethyl alcohol and hydrogen chloride in chloroform solution, into tellurium *O*-ethyl β-diketone trichlorides (XIV, J., 1921, **119**, 610), the *cyclo*telluripentanedione ring becomes incipiently fixed in the unstable enolised form (XIII) by alkylation of the hydroxyl group, the strained ring being then broken by hydrogen chloride at one of the tellurium–carbon linkings:

(XIII.)   (XIV.)

*cyclo*Telluri-4-alkylpentanedione dichlorides do not undergo this transformation, because the already feeble tendency to enolisation has completely disappeared with the introduction of the 4-alkyl group.

EXPERIMENTAL.

cyclo*Telluri*-4:4-*dimethylpentane*-3:5-*dione* 1:1-*dichloride* (formula X) forms colourless, transparent, brittle, prismatic needles from acetone, m. p. 194° with intumescence and blackening; it is less soluble in cold chloroform or carbon tetrachloride: 0·1060 gave 0·0933 AgCl, whence Cl = 21·77. $C_7H_{10}O_2Cl_2Te$ requires Cl = 21·85 per cent.

3:3-Dimethylacetylacetone was prepared from 61 gms. of

sodium 3-methylacetylacetone and 250 gms. of methyl iodide by heating in a glass bottle in the rotating autoclave at 120—160°/220 lb. per sq. in. for 4 hours; sodium iodide was removed and the filtrate dried with sodium sulphate and fractionated; the product boiled at 61—62°/9 mm. and melted at 26°: total yield 23 gms. (compare *Bull. Soc. chim.*, 1892, [iii], **7**, 783; J., 1894, **65**, 824; *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 491).

Preparation: Tellurium tetrachloride (13 gms.) and dimethylacetylacetone (11 gms.) in 100 c.c. of pure chloroform, were refluxed for $2\frac{3}{4}$ hours, hydrogen chloride being evolved. The pale yellow filtrate from tellurium was concentrated in a desiccator and the crystals were washed with cold carbon tetrachloride and chloroform; the filtrates were again concentrated; yield 60 per cent. of dichloride as sole product.

cyclo*Telluro*-4 : 4-*dimethylpentane*-3 : 5-*dione* (formula IV) forms transparent, lemon-yellow, refractive prisms from benzene; golden-yellow needles from alcohol; serrated needles from water: m. p. 124—125°, sublimation point in a vacuum 105°. The solubilities were considerable in cold chloroform and warm organic solvents and moderate in cold water or alcohol: 0·1874 gave 0·0648 H_2O, 0·2276 CO_2; 0·3792 gave 0·1918 Te; whence C = 33·13; H = 3·87; Te = 50·58. *M* (ebullioscopic method in benzene, *c* = 0·726, 1·390) = 270, 275. $C_7H_{10}O_2Te$ requires C = 33·14; H = 3·98; Te = 50·27 per cent.; *M* = 253·5. This compound is neither acidic to sodium hydroxide nor enolic to ferric chloride. It was prepared from the powdered dichloride (8·7 gms.) and 12·2 gms. of potassium metabisulphite in 70 c.c. of cold water; the yield was quantitative, the aqueous filtrates being extracted with chloroform.

Oximes of cyclo*Telluropentane*-3 : 5-*diones*.

1. cyclo*Telluropentane*-3 : 5-*dionedioxime* (formula I) forms pale yellow needles in voluminous masses from hot water or glacial acetic acid; m. p. indefinite; it blackened at 180—190° and tellurium was eliminated violently at 207°: 0·2037 gave 18·9 c.c. moist * N_2 at 14·5°/760·5 mm., whence N = 10·85. $C_5H_8O_2N_2Te$ requires N = 10·96 per cent.

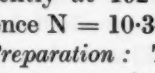
Preparation: 1 Gm. of hydroxylamine sulphate in 45 c.c. of water containing sodium acetate was added to 0·5 gm. of tellurium acetylacetone in 45 c.c. of boiling water; the oxime crystallised on cooling.

2. cyclo*Telluro*-4-*ethylpentane*-3 : 5-*dionedioxime* (formula II) separated in golden-yellow platelets from acetylacetone, and in

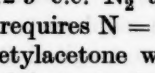
* Moist N_2 throughout.

shortened needles from hot water; it was sparingly soluble in volatile organic solvents, darkened at 173°, and decomposed violently at 192°: 0·1413 gave 12·9 c.c. N_2 at 17°/745·5 mm., whence N = 10·34. $C_7H_{12}O_2N_2Te$ requires N = 9·88 per cent.

Preparation: Tellurium ethylacetylacetone was treated with a large excess of hydroxylamine sulphate in boiling water; the solution was neutralised with sodium hydroxide and after 10 minutes allowed to cool.



(XV.)



(XVI.)

3. cyclo*Telluro*-2:4-*dimethylpentane*-3:5-*dione*-5-*monoxime* (formula XV), obtained in minute yellow needles from hot water or benzene, darkened at 140°, became black at 164°, and broke down at 168°: 0·1604 gave 7·75 c.c. N_2 at 15°/733·4 mm., whence N = 5·43. $C_7H_{11}O_2NTe$ requires N = 5·22 per cent.

Preparation: 0·7 Gm. of tellurium 3-methylpropionylacetone in 100 c.c. of hot water was added to 2 gms. of hydroxylamine sulphate in 35 c.c. of water containing sodium acetate till the solution was nearly neutral to litmus; it was then warmed for a few minutes and cooled.

4. cyclo*Telluro*-2:4-*dimethylpentane*-3:5-*dionedioxime* (formula XVI), a yellow, crystalline powder from hot acetylacetone, sparingly soluble in hot water and insoluble in volatile organic solvents, darkens at 173° and decomposes violently at 198°: 0·1497 gave 13·1 c.c. N_2 at 12°/756 mm., whence N = 10·28. $C_7H_{12}O_2N_2Te$ requires N = 9·88 per cent.

Preparations: i. Along with a small proportion of the monoxime by effecting the foregoing oximation in slightly alkaline solution (NaOH). ii. The monoxime was dissolved in hot aqueous alcohol and treated with hydroxylamine.

The mono- and di-oximes dissolved in aqueous sodium hydroxide to yellow solutions stable in the cold, decomposed by warming.

5. α- *and* β-cyclo*Telluro*-2-*ethylpentane*-3:5-*dionedioximes* (formulæ VI, VII, and VIII).—The *α-dioxime*, obtained in minute, canary-yellow needles in nacreous masses, is readily soluble in hot benzene, and has m. p. 149° (decomp.); its solubility in organic solvents is greater than that of the β-isomeride: 0·2071 gave 18·6 c.c. N_2 at 20·2°/740 mm., whence N = 9·94. $C_7H_{12}O_2N_2Te$ requires N = 9·88 per cent.

The *β-dioxime* forms yellow needles similar to the preceding but of lighter tint. It is practically insoluble in boiling benzene, crystallises from boiling alcohol, darkens at 170°, and intumesces

at 183° : 0·1234 gave 11·1 c.c. N_2 at 20°/742·7 mm., whence N = 10·00 per cent.

Preparation : A slightly alkaline solution of 10 gms. of hydroxylamine sulphate in aqueous sodium hydroxide was added to 3·5 gms. of tellurium *n*-butyrylacetone in 100 c.c. of warm alcohol, water being added until the two layers mixed. After 10 minutes' boiling, the solution was cooled during 12 hours; the first crops to separate consisted of α-dioxime, the intermediate crops were mixtures, and finally the β-isomeride was deposited. The two oximes were separated by boiling benzene, the proportions being α : β = 5 : 1. Both isomerides were slightly soluble in hot water and dissolved in cold aqueous sodium hydroxide to yellow solutions which blackened on warming.

6. cyclo*Telluro* - 4 : 4 - *dimethylpentane* - 3 : 5 - *dione*- 5 -*monoxime* (formula III) separated in orange-yellow needles, m. p. 183—184° (decomp.), from benzene, also from alcohol in pale yellow needles or orange prisms, m. p. 180°, sublimable in a vacuum : 0·2650 gave 12·5 c.c. N_2 at 17·5°/733 mm., whence N = 5·24. $C_7H_{11}O_2NTe$ requires N = 5·22 per cent.

Preparation : An excess of hydroxylamine sulphate in aqueous sodium acetate (still acidic) was added to tellurium 3 : 3-dimethylacetylacetone in boiling water. The *monoxime*, which separated after a few minutes' warming, was crystallised from hot benzene.

7. cyclo*Telluro*-4 : 4-*dimethylpentane*-3 : 5-*dionedioxime* (formula V), minute, golden-yellow needles from acetylacetone, is practically insoluble in water, benzene, and other volatile solvents; it decomposes at 235° : 0·1413 gave 11·6 c.c. N_2 at 9°/756 mm., whence N = 9·80. $C_7H_{12}O_2N_2Te$ requires N = 9·88 per cent.

Preparations : i. The foregoing oximation with larger excess of sodium acetate and warming for a few minutes yielded slowly the mono- and di-oximes, which were separated by boiling benzene, the latter product being insoluble.

ii. A large excess of hydroxylamine sulphate, rendered alkaline with aqueous sodium hydroxide, was added to a boiling aqueous-alcoholic solution of the monoxime.

Both oximes dissolved in aqueous caustic alkali to yellow solutions, which deposited tellurium on warming.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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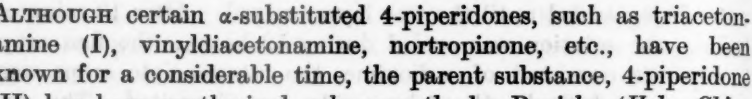
CCXII.—*Synthesis of 4-Tetrahydroquinolone and a new Synthesis of 4-Methoxyquinoline.*

By GEORGE ROGER CLEMO and WILLIAM HENRY PERKIN, junr.

ALTHOUGH certain α-substituted 4-piperidones, such as triacetonamine (I), vinyldiacetonamine, nortropinone, etc., have been known for a considerable time, the parent substance, 4-piperidone (II) has been synthesised only recently by Ruzicka (*Helv. Chim. Acta*, 1920, **3**, 806, 818; 1922, **5**, 715). Ruzicka, however, was unable to isolate the free base on account of its tendency to polymerise, but he prepared its stable benzylidene derivative.

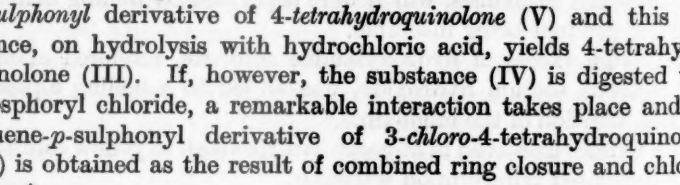


(I.) (II.) (III.)

The literature contains, however, no mention of 4-tetrahydroquinolone (III), although it is obvious that such a substance must be of considerable interest, not only on account of its possible physiological properties, but also owing to the fact that it possesses a very reactive system which is readily attacked at three points. It should therefore be valuable as a starting point for a variety of synthetical operations. We have now succeeded in synthesising this substance. In the first place, toluene-*p*-sulphonanilide, $C_6H_5\cdot NH\cdot SO_2\cdot C_6H_4Me$, is condensed with β-chloropropionic acid and thus converted into the *toluene*-p-*sulphonyl* derivative of β-*anilinopropionic acid* (IV).

(IV.) $C_6H_5\cdot N(SO_2\cdot C_6H_4Me)\cdot CH_2\cdot CH_2\cdot CO_2H$.

When this substance is digested, in xylene solution, with phosphoric oxide, ring closure occurs with the formation of the *toluene*-p-*sulphonyl* derivative of 4-*tetrahydroquinolone* (V) and this substance, on hydrolysis with hydrochloric acid, yields 4-tetrahydroquinolone (III). If, however, the substance (IV) is digested with phosphoryl chloride, a remarkable interaction takes place and the toluene-*p*-sulphonyl derivative of 3-*chloro*-4-tetrahydroquinolone (VI) is obtained as the result of combined ring closure and chlorination.*



(V.) (VI.)

* The abbreviation $-SO_2X$ will be used throughout this communication for $-SO_2\cdot C_6H_4Me$.

It was at first thought possible that the substance (III) might be obtained by condensing aniline with β-chloropropionic acid followed by ring closure but, on trying the experiment, only uninviting mixtures resulted.

In this connexion, it is of interest to note that β-anilinopropionic acid has been prepared by Bischoff (*Ber.*, 1892, **25**, 2351) from aniline and β-iodopropionic acid, but, apart from the fact that Walden (*Z. physikal. Chem.*, 1892, **10**, 649) has determined its electrical conductivity, it does not appear to have been further investigated. This is evidently due to the difficulty of preparing β-anilinopropionic acid by this method.

The formation of the chloro-derivative (VI) under the conditions described is difficult to understand because, although phosphoryl chloride has been extensively used as an agent for ring closure, simultaneous chlorination does not appear to have been previously observed. Thus, for example, when β-phenoxypropionic acid is treated with phosphoryl chloride, 4-chromanone is produced and not a chloro-derivative.

With regard to the position of the chlorine atom in (VI), the fact that when the substance is treated with concentrated sulphuric acid hydrogen chloride is liberated in the cold, indicates that the chlorine atom cannot be situated in the benzene ring of the quinolone nucleus. This deduction is confirmed by the fact that the substance (VI) is readily reduced both in alkaline and acid solution and indeed by simply warming with hydrochloric acid (see below) with the formation of substances free from chlorine. The chlorine atom cannot be attached to nitrogen, because the substance (VI) may be heated with alcoholic diethylamine or with diethylaniline or with potassium iodide without being appreciably changed.

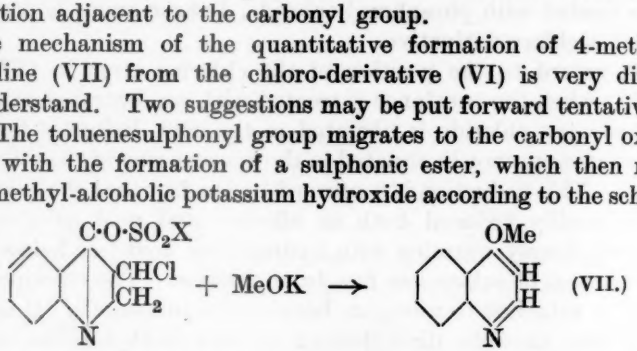
The most extraordinary property of (VI) is the fact that it is readily reduced to 4-tetrahydroquinolone with the simultaneous elimination of the toluene-*p*-sulphonyl group when it is boiled with concentrated hydrochloric acid. This appears to be the first recorded case of the replacement of chlorine by hydrogen by treatment with hydrochloric acid. The replacement of bromine by hydrogen in bromo-ketones and in substances such as bromoacetoacetic ester and bromomalonic ester, which contain the bromine atom adjacent to the carbonyl group, has been observed, but no mention is made of such a change being brought about by the agency of hydrochloric acid. If the polar hypothesis is applied to this case, it may be assumed that the combined effect of the $>N\cdot SO_2\cdot C_6H_4Me$ and carbonyl groups in the toluenesulphonyl derivative of 4-tetrahydroquinolone is so strong that a hydrogen atom of the β-CH_2-group becomes easily replaced by chlorine and,

vice versa, that the chlorine so introduced is, in its turn, readily replaceable by hydrogen.

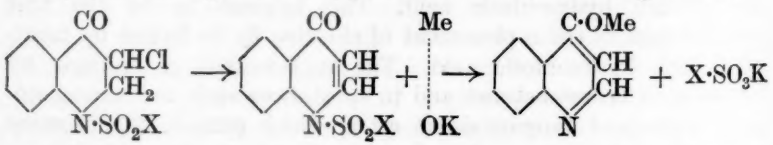
Curious results were also obtained during the investigation of the action of alkalis on the substances (V) and (VI). On boiling the unchlorinated substance (V) with methyl-alcoholic potassium hydroxide, it does not lose the toluenesulphonyl group, but is converted into an isomeric substance of unknown constitution. On the other hand, the chlorinated substance (VI), when digested with methyl-alcoholic potassium hydroxide, is converted quantitatively into 4-methoxyquinoline (VII) with elimination of the toluenesulphonyl group. Elimination of the toluenesulphonyl group under these conditions does not appear to have been previously observed. Taken in conjunction with the behaviour of this substance (VI) with hydrochloric acid (see above), it would appear that the removal of the toluenesulphonyl group is in some way connected with the presence of the chlorine atom in the β-position adjacent to the carbonyl group.

The mechanism of the quantitative formation of 4-methoxyquinoline (VII) from the chloro-derivative (VI) is very difficult to understand. Two suggestions may be put forward tentatively:

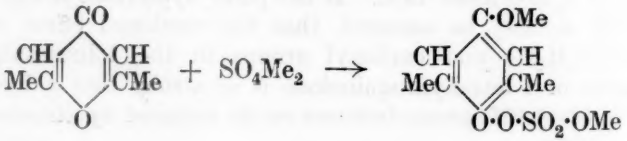
(i) The toluenesulphonyl group migrates to the carbonyl oxygen atom with the formation of a sulphonic ester, which then reacts with methyl-alcoholic potassium hydroxide according to the scheme



(ii) The chlorinated substance (VI) first loses hydrogen chloride with the formation of an unstable dihydro-derivative which, in order to pass into the stable quinoline configuration, reacts with methyl-alcoholic potassium hydroxide in the following manner:



This kind of change is reminiscent of the addition of methyl sulphate to dimethylpyrone (Baeyer, *Ber.*, 1910, **40**, 2337)



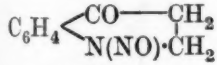
(compare also Hamilton and Robinson, J., 1916, **109**, 1029). Against the view that the first stage is the elimination of hydrogen chloride, must be put the observation that, when the action of methyl-alcoholic potassium hydroxide on (VI) is incomplete, a mixture is formed of basic substances which contain considerable quantities of chlorine but no sulphur and therefore are free from the toluene-sulphonyl group. This observation suggests that the first stage in the action of methyl-alcoholic potassium hydroxide (and possibly also of hydrochloric acid) on (VI) is the removal of the toluene-sulphonyl group.

The literature contains apparently only one reference to 4-methoxyquinoline. Meyer (*Monatsh.*, 1906, **27**, 257) prepared this substance from 4-chloroquinoline and sodium methoxide, and describes it as melting at 31° and yielding a mercurichloride melting at 188—190°, whereas we find that it melts at 39—40° and that the melting point of the mercurichloride is 202°.

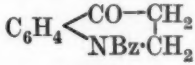
The synthesis of 4-tetrahydroquinolone by the method described above suggested that 2-methyltetrahydroquinolone should be similarly formed if the β-chloropropionic acid were replaced by β-chlorobutyric acid. All attempts to condense toluene-*p*-sulphonanilide with β-chlorobutyric acid have, however, been unsuccessful, the anilide has always been recovered unchanged and the β-chlorobutyric acid apparently completely converted by elimination of hydrogen chloride into crotonic acid.

Properties of 4-Tetrahydroquinolone (III).

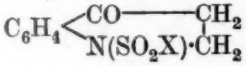
4-Tetrahydroquinolone differs from 4-piperidone (II) in being a stable substance which melts at 44°, distils at 195°/20 mm., and does not appear to change on keeping. It contains three very reactive groups, namely the >NH, the >CO and the β-CH_2< groups. The presence of the >NH group is evidenced by the fact that the substance yields a nitroso-derivative (VIII) and that it reacts with benzoyl chloride and with toluene-*p*-sulphonyl chloride to yield the derivatives (IX) and (X).



(VIII.)



(IX.)



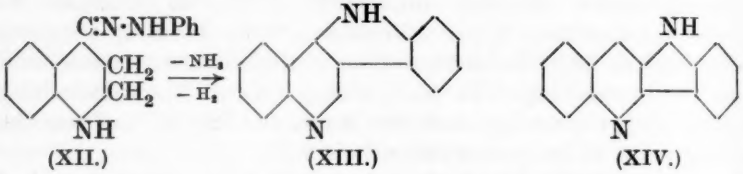
(X.)

Several interesting condensations have been carried out with 4-tetrahydroquinolone which indicate that this substance may prove to be very useful as a reagent for synthetical work. The following examples illustrate this point:

(i) 4-Tetrahydroquinolone reacts readily with aldehydes and

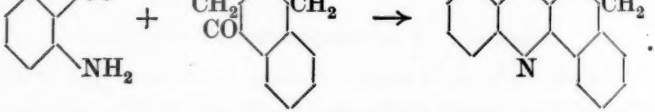
gives, for example, with benzaldehyde a characteristic 3-*benzylidene* derivative.

It combines with phenylhydrazine, and the *phenylhydrazone* (XII), on treatment with dilute sulphuric acid, undergoes the Fischer indole transformation. Instead, however, of the reaction proceeding normally with the formation of a dihydro-derivative, simultaneous oxidation takes place with the loss of two atoms of hydrogen; the strongly basic substance (XIII) thus obtained we propose to name 3 : 4-*quinindoline*, because it is isomeric with ordinary quindoline (2 : 3-quinindoline XIV).

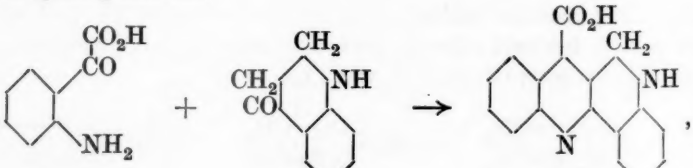


(XII.) (XIII.) (XIV.)

(ii) von Braun and Wolff (*Ber.*, 1922, **55**, 3675) have recently shown that α-tetralone condenses readily with isatic acid to yield 5 : 6-dihydro-α-naphthacridine-7-carboxylic acid, a substance which resembles strychnine in its physiological properties (compare von Braun and Stuckenschmidt, *Ber.*, 1923, **56**, 1724).



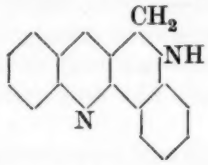
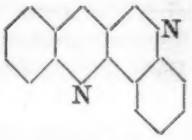
In view of this observation, it seemed to us that it would be of interest to prepare the analogous condensation product from 4-tetrahydroquinolone,



because this substance, owing to the presence of the two nitrogen atoms, might resemble strychnine still more closely than von Braun's acid.

We have, however, in the meantime, not been able to isolate the carboxylic acid figured above in the pure state. But when isatin and 4-tetrahydroquinolone are condensed and the product is heated

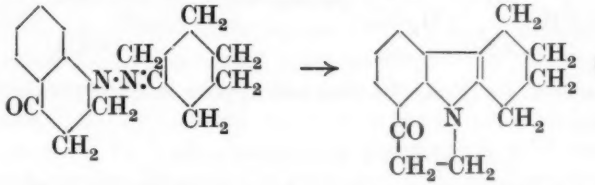
under reduced pressure at 210°, carbon dioxide is eliminated and a base distils which is evidently *dihydro*-2 : 3-*quinoquinoline* * (XV) and this, on distillation over lead oxide, loses two atoms of hydrogen with the formation of 2 : 3-*quinoquinoline* (XVI).

(XV.)   (XVI.)

Both these substances have pronounced basic properties and yield a number of interesting derivatives which are at present under examination.

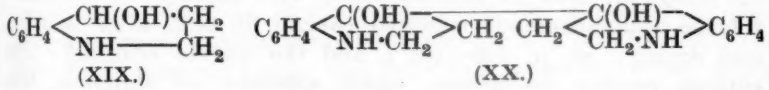
The investigation of the physiological properties of these and several of the other substances described in this communication is also in progress.

(iii) The nitroso-derivative of 4-tetrahydroquinolone (VIII) is converted, on reduction with zinc dust in the presence of *cyclo*hexanone, into 1-cyclo*hexylideneamino*-4-*tetrahydroquinolone* (XVII) and this, on warming with dilute sulphuric acid, readily undergoes the Fischer indole transformation with the formation of *tetrahydrocarbazole*-9 : 8-*anhydropropionic acid* (XVIII) :

(XVII.)  (XVIII.)

This anhydro-derivative has basic properties and, in virtue of its ketone group, condenses readily with phenylhydrazine, yielding a pale yellow hydrazone melting at 191°.

4-Tetrahydroquinolone is readily reduced by sodium amalgam with the formation of a mixture of 4-*hydroxytetrahydroquinoline* (XIX) and the corresponding pinacol, 4 : 4′-*dihydroxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-4 : 4′-*diquinolyl* (XX) :



(XIX.) (XX.)

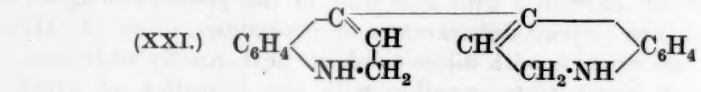
4-Hydroxytetrahydroquinoline is a strong base which is readily soluble in water and yields a diacetyl derivative.

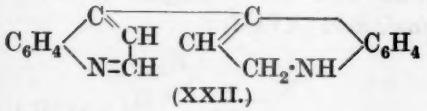
* It is remarkable that the product of this change should be the dihydro-derivative and that oxidation does not occur as in the case of the formation of (XIII).

The pinacol (XX) also is a strong base. Since it contains two asymmetric carbon atoms, it should exist in two modifications but only one isomeride has been isolated; if the other is formed at all, it must be in very small quantities. An analogous case has been described by Freudenberg and Orthner (*Ber.*, 1922, **55**, 1748), who, on reducing flavanone with aluminium amalgam, obtained the simple reduction product—flavanol—as well as considerable quantities of the pinacol, which again was only isolated in one modification.

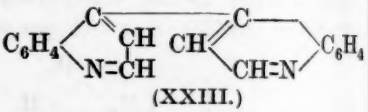
When the pinacol (XX) is dissolved in cold concentrated sulphuric acid it loses 2 mols. of water with the formation of 1:2:1′:2′-*tetrahydro*-4:4′-*diquinolyl* (XXI), a crystalline base which yields a diacetyl derivative. If the methyl-alcoholic solution of (XXI) is boiled, oxidation takes place and the dihydro-derivative (XXII) is obtained; if this is kept in contact with methyl alcohol for several days, further oxidation occurs with the formation of 4:4′-*diquinolyl* (XXIII).

(XXI.)





(XXII.)



(XXIII.)

This series of substances does not appear to have previously been described.

Experimental.

Toluene-p-*sulphonyl*-β-*anilinopropionic Acid* (IV).—To toluene-*p*-sulphonanilide (*Ber.*, 1879, **12**, 1348) (74 gms.), dissolved in caustic soda (150 c.c. of 8 per cent.; 1 equiv.), a cold solution of β-chloropropionic acid (32·5 gms.) in caustic soda (150 c.c. of 8 per cent.) was added, and the solution gently refluxed for about 5 hours, small, oily drops of toluene-*p*-sulphonanilide soon rendering the initial clear solution milky. The reaction mixture was cooled for about an hour in ice-cold water with stirring, the granular toluene-*p*-sulphonanilide collected (weight 40 gms. after washing and drying; m. p. 100—102°), and the filtrate acidified. The copious gummy precipitate, which solidified on standing, was collected, ground, washed with water, and dried on the water-bath. The product (O), 42—43 gms., m. p. 135—138°, was boiled with benzene (140 c.c.), and the solution filtered from a trace of an insoluble acid; on cooling, 37·5 gms. of colourless, hair-like prisms separated, m. p. 143°, and 144° after recrystallisation (Found:

C = 60·41; H = 5·53. $C_{16}H_{17}O_4NS$ requires C = 60·2; H = 5·3 per cent.).

Toluene-*p*-sulphonyl-β-anilinopropionic acid (IV) is readily soluble in cold aqueous sodium carbonate, but almost insoluble in light petroleum, in both of which respects it differs from toluene-*p*-sulphonanilide. Its *methyl* ester, prepared by warming it for 5 minutes on the water-bath with 10 per cent. methyl-alcoholic hydrochloric acid, crystallises from methyl alcohol in colourless, stout, well-defined, tetragonal prisms, m. p. 61—62° (Found: C = 61·56; H = 5·74. $C_{17}H_{19}O_4NS$ requires C = 61·3; H = 5·7 per cent.).

It has been stated above that a trace of a by-product (O) insoluble in benzene resulted during the condensation of toluene-*p*-sulphonanilide and β-chloropropionic acid under the conditions employed. If the conditions used above in this condensation are varied by dropping the β-chloropropionic acid, dissolved in an equivalent of aqueous sodium carbonate, during an hour into the solution of the toluene-*p*-sulphonanilide in caustic soda, about one-half of the condensation product consists of the acid insoluble in benzene. This substance (O) crystallises from methyl alcohol in thin, colourless prisms, m. p. 213° (Found: C = 58·21, 58·20; H = 5·19, 5·12 per cent.). The molecular weight (mean of three results by Rast's method) = 662, which indicates that the acid has a molecular weight about double that (319) of (IV).

This acid (O) is intimately related to (IV), since treatment with methyl-alcoholic hydrochloric acid produces the methyl ester, m. p. 61—62°. Again, when the acid (O) (5 gms.) is dissolved in dilute caustic soda, and the solution acidified after standing, or, better, warming for a short time, 4·8 gms. (*ca.*) of (IV) result.

When, however, the acid (O) is treated with phosphoryl chloride under the conditions employed to convert (IV) into (VI) (see p. 1616), ring closure is not effected to any extent, since treatment of the reaction mixture with methyl-alcoholic potash followed by acidification results in the isolation of (IV). Treatment of the acid (O) with phosphoric oxide in xylene does, however, result in the formation of a certain amount of (V). The acid (O) is unchanged by a short boiling with aniline, and up to the present no clear idea of its constitution has been formed; but from the molecular weight, analytical results, and experimental evidence it seems almost certain that (O) is formed in some way from two molecules of (IV) and a molecule of water, since $2C_{16}H_{17}O_4NS,H_2O$ requires C = 58·6; H = 5·18; N = 4·27 per cent.

Action of (a) *Phosphoric Oxide and* (b) *Phosphoryl Chloride on Toluene*-p-*sulphonyl*-β-*anilinopropionic Acid* (IV).—(a) The substance (IV) (6·4 gms.) was dissolved in dry xylene (50 c.c.), phos-

phoric oxide (5·6 gms., *i.e.*, 2 mols.) added, the mixture gently refluxed for 2 hours, the xylene removed in steam, and the residue treated with sodium carbonate. The light brown, amorphous, non-acidic product was collected, and dried on the steam-bath, when 3·5 gms. of crude material resulted which, when crystallised from methyl alcohol, gave 2 gms. of faintly brown, well-defined prisms, m. p. 138—140°, and at 140—141° after recrystallisation [Found: C = 64·05; H = 5·24. $C_{16}H_{15}O_3SN$ (V) requires C = 63·8; H = 5·0 per cent.].

On acidifying the sodium carbonate filtrate 1·6 gms. of (IV) were regained. The compound (V) dissolves in concentrated sulphuric acid to an almost colourless, non-fluorescent solution (compare action of sulphuric acid on VI, below).

(b) A solution of the substance (IV) (20 gms. of the uncrystallised material) in phosphoryl chloride (60 c.c.) was heated for 15 minutes in the water-bath, the excess of the oxychloride (45 c.c. approx.) was then removed from the reddish-brown solution by distillation under reduced pressure, and the viscid residue poured on to ice and water. After standing for a short time, the mixture was heated for a few minutes in the water-bath, when a heavy oil resulted which set to a granular solid on shaking and cooling. This product, which smelt of toluenesulphonyl chloride, was collected (filtrate A) and dissolved in methyl alcohol, when 9—10 gms. of colourless, glistening prisms, m. p. 121—123°, separated on standing, and a second crystallisation raised the melting point to 124° [Found: C = 59·7; H = 4·36; N = 4·8; Cl = 10·9; S = 10·2. $C_{16}H_{14}O_3NClS$ (VI) requires C = 60·0; H = 4·5; N = 4·5; Cl = 10·6; S = 9·5 per cent.].

On making the filtrate (A) alkaline and extracting with benzene, a small amount of a mixture of bases resulted from which some 4-tetrahydroquinolone could be isolated, but the composition of the basic mixture has not yet been fully investigated. The substance (VI) dissolves in concentrated sulphuric acid to give a colourless solution which almost at once becomes pink, and in about a minute an intense violet colour results and hydrogen chloride is liberated.

4-*Tetrahydroquinolone* (III).—The chloro-derivative (VI) * (20 gms.) was gently refluxed with a mixture of acetic acid (100 c.c.) and hydrochloric acid (130 c.c.) for 4½ hours, the acids were then removed by distillation under reduced pressure from the water-bath, and the viscid, reddish-brown gum was shaken with caustic

* Similar conditions have been used for the hydrolysis of (V) and also yielded 4-tetrahydroquinolone, but as large amounts of this substance have been made from (VI), and, further, as the hydrolysis of (VI) is the more interesting one, it alone will be described.

soda (150 c.c. of 8 per cent.), which neutralised any remaining hydrochloric acid and also dissolved the toluenesulphonic acid formed during the hydrolysis. The heavy oil which had separated was extracted with ether, the extract dried and fractionated, when 8—8·5 gms. of a stable, viscid, orange-coloured oil passed over at 195°/20 mm. and quickly solidified to a yellow, crystalline mass, m. p. 44°. This was sparingly soluble in boiling light petroleum, and pale yellow, thin leaflets, m. p. 44°, separated on cooling (Found : C = 73·87; H = 6·26; N = 9·56. C_9H_9ON requires C = 73·5; H = 6·12; N = 9·5 per cent.). It is slightly soluble in cold water and very easily soluble in dilute acids. Its solutions, especially in alcohol, in which it is very readily soluble, exhibit a pale green fluorescence.

Benzoyl-4-tetrahydroquinolone (IX), readily formed from (III) and benzoyl chloride in presence of caustic soda or pyridine, crystallises from methyl alcohol in large, colourless plates, m. p. 122° (Found : C = 76·63; H = 5·12; N = 5·55. $C_{16}H_{13}O_2N$ requires C = 76·5; H = 5·2; N = 5·6 per cent.).

Again, when (III) (1·5 gms.) and toluenesulphonyl chloride (2 gms.) are heated in the water-bath with stirring for ½ hour in presence of an equivalent of dilute caustic soda, the *N-toluene-p-sulphonyl* derivative (V) is formed. This crystallises from methyl alcohol in colourless, glistening prisms, melts at 141°, and is identical with the substance (V) obtained as described on p. 1616.

3-Benzylidene-4-tetrahydroquinolone (XI).—4-Tetrahydroquinolone (1·5 gms.), benzaldehyde (1·1 gms.), ethyl alcohol (5 c.c.), and caustic soda (0·05 gm.) were heated at 80°, with shaking at intervals, for 20 hours. Water was added, and the resulting orange-coloured gum stirred with a little methyl alcohol, when a light yellow solid separated. This was collected and crystallised from methyl alcohol, from which the *benzylidene* derivative separated in pale yellow plates, m. p. 214° (Found : C = 81·6; H = 5·65. $C_{16}H_{13}ON$ requires C = 81·7; H = 5·5 per cent.). The solution of the substance in concentrated sulphuric acid is almost colourless.

4-Methoxyquinoline.—When the sulphonyl derivative (V) (6 gms.) was refluxed for 6 hours with methyl-alcoholic potash (20 c.c. of 25 per cent.), the bulk of the alcohol distilled off, and water added, a yellow solution resulted which was converted into a stiff jelly on the addition of acids or brine. On heating, this jelly changed to an amorphous solid, which was collected and dissolved in a little boiling acetic acid. The precipitate obtained on cooling was washed with alcohol and dried, when a pale grey powder resulted which melted indefinitely at 135—150° (Found : C = 63·2; H = 5·0. $C_{16}H_{15}O_3NS$ requires C = 63·8; H = 5·0 per cent.).

This substance still contains the sulphonyl residue, is almost insoluble in alcohol, and is isomeric with (V), from which, however, it differs in being almost insoluble in alcohol, and in other properties. So far no clue has been obtained as to its constitution.

Preparation of 4-Methoxyquinoline.—The chloro-compound (VI) (21 gms.) was refluxed for 6 hours with methyl-alcoholic potash (50 c.c. of 25 per cent.). Water was then added, the precipitated oily base extracted with ether and the extract dried and fractionated, when 9 gms. passed over at 167°/20 mm. and, after cooling in ice, the pure 4-*methoxyquinoline* solidified to a nearly colourless, crystalline solid, m. p. 39—40° (Found: C = 75·2; H = 5·7. $C_{10}H_9ON$ requires C = 75·5; H = 5·7 per cent.).

This base gives a *methiodide* which crystallises from methyl alcohol in large, pale yellow, flat plates; these become opaque on drying on the water-bath and melt with decomposition at 145° (Found: N = 4·8. $C_{11}H_{12}ONI$ requires N = 4·65 per cent.).

4-Methoxyquinoline yields a *mercurichloride*, colourless, silky needles, m. p. 201—202° (decomp.), from water.

3 : 4-*Quinindoline.*—4-Tetrahydroquinolone (3 gms.), phenylhydrazine (2·1 gms.), ethyl alcohol (5 c.c.), and two drops of acetic acid were heated together at 80° for 1½ hours. The crystalline mass of the hydrazone (XII) obtained on keeping was ground, and washed with a little methyl alcohol. From methyl alcohol solution it separated in very pale biscuit-coloured plates, m. p. 110° (Found: C = 76·0; H = 6·2; N = 17·6. $C_{15}H_{15}N_3$ requires C = 76·0; H = 6·3; N = 17·7 per cent.).

This 4-*tetrahydroquinolonephenylhydrazone* (1 gm.) was mixed with sulphuric acid (10 c.c. of 20 per cent. H_2SO_4) and heated, with stirring, in the water-bath, when an orange-coloured liquid resulted in 5 minutes. After heating for a further 7 minutes, a pale yellow, crystalline precipitate began to separate and increased in amount during the next 10 minutes. Water was added and the pale yellow mass collected and treated with ammonia, when a colourless solid (0·4 gm.) resulted. This substance crystallised from its concentrated methyl alcohol solution, which showed a light reddish-blue fluorescence, in irregular, colourless prisms.

3 : 4-*Quinindoline* melts and sublimes above 320° (Found: C = 82·2; H = 4·4. $C_{15}H_{10}N_2$ requires C = 82·60; H = 4·6 per cent.). It dissolves in hot dilute hydrochloric acid and, on cooling, the *hydrochloride* separates in thin, colourless prisms. The base gives a sparingly soluble *chloroplatinate*. Its colourless sulphuric acid solution shows no trace of fluorescence (compare Lawson, Perkin, and Robinson, J., 1924, **125**, 634).

Tetrahydrocarbazole-9 : 8-*anhydropropionic Acid* (XVIII).—4-Tetrahydroquinolone (1 gm.) was dissolved in acetic acid (5 c.c.) and concentrated hydrochloric acid (3 drops) and a little ice were added, and then aqueous sodium nitrite (1·5 c.c. of 25 per cent.) was dropped in with stirring, when the whole set to a pale yellow, crystalline mass of *nitroso*-4-*tetrahydroquinolone* (VIII). Water was added, the solid collected, and crystallised from a little methyl alcohol, when almost colourless, thin prisms, m. p. 98°, separated (Found : C = 61·3; H = 4·9. $C_9H_8O_2N_2$ requires C = 61·3; H = 4·5 per cent.).

This nitroso-derivative (not recrystallised) was now dissolved in acetic acid (10 c.c.), mixed with *cyclo*hexanone (2 c.c.), and then zinc dust (2 gms. of 90 per cent.) added in portions with stirring, the temperature meanwhile, and for 5 minutes afterwards, being kept at 35—40°. The mixture was rapidly filtered, the zinc residues were extracted with a little acetic acid, and a considerable volume of water was added to the combined filtrates, when, in a few minutes, a yellow, crystalline precipitate (0·7 gm.) was obtained which melted at 108—110°. 1-cyclo*Hexylideneamino*-4-*tetrahydroquinolone* (XVII) crystallises from methyl alcohol, in which it is easily soluble, in bright canary-yellow prisms, m. p. 112° (Found : C = 74·5; H = 7·4; N = 11·5. $C_{15}H_{18}ON_2$ requires C = 74·4; H = 7·4; N = 11·6 per cent.). It remains unchanged on heating for a short period with acetic acid, treatment which usually leads to indole formation.

Tetrahydrocarbazole-9 : 8-*anhydropropionic Acid* (XVIII).—The pale yellow solution of (XVII) (1 gm.) in sulphuric acid (10 c.c. of 20 per cent.) was heated for 15 minutes in the water-bath, a copious brown, crystalline precipitate separating. Ice and excess of ammonia were then added and the solid (0·9 gm.) was crystallised from methyl alcohol, from which the acid separated in pale brown, flat, opaque plates, m. p. 135—136° (Found : C = 80·1; H = 6·7. $C_{15}H_{15}ON$ requires C = 80·1; H = 6·7 per cent.).

This acid dissolves in sulphuric acid to a pale yellow solution exhibiting a pale green fluorescence which disappears on the addition of a trace of nitric acid. When an alcoholic solution of the substance, containing a trace of acetic acid, is boiled with an equivalent of phenylhydrazine the solution becomes filled at once with a crystalline precipitate of the *phenylhydrazone*, which crystallises from alcohol in thin, pale yellow prisms, m. p. 191° (Found : C = 80·1; H = 6·7. $C_{21}H_{21}N_3$ requires C = 80·0; H = 6·7 per cent.). This phenylhydrazone dissolves in sulphuric acid to a deep yellow solution.

Dihydro-2 : 3-*quinoquinoline* (XV) *and* 2 : 3-*Quinoquinoline* (XVI).—A solution of 4-tetrahydroquinolone (6 gms.), isatin (6 gms.), and

caustic potash (7·8 gms.) in water (7·8 c.c.) and alcohol (15 c.c.) was gently refluxed for 20 hours. Water and excess of acetic acid precipitated from the brown solution a substance resembling red phosphorus in appearance which, after being washed with water and dried on the water-bath, gave 10 gms. of a red powder, practically insoluble in alcohol and acetic acid, although readily soluble in alkalis.*

This red powder, heated in quantities of 4 grams in small distilling flasks, melted at 210° with vigorous decomposition and evolution of carbon dioxide and water. When the frothing had ceased the pressure was reduced and, on heating, a pale yellow oil passed over and at once solidified in the receiver. The product (3 gms.) after being ground with dilute caustic soda, and crystallised from methyl alcohol, gave pale yellow, thin prisms of *dihydro*-2 : 3-*quinoquinoline*, which became opaque when dried on the water-bath. This substance softens at 230° and melts at 235—237° (Found : C = 83·5; H = 5·1. $C_{16}H_{12}N_2$ requires C = 82·8; H = 5·2 per cent.).

Dihydro-2 : 3-quinoquinoline is a fairly strong base which dissolves in dilute hydrochloric acid, giving a yellow solution with a green fluorescence. Its pale yellow solution in concentrated sulphuric acid shows a light blue fluorescence. It is somewhat sparingly soluble in benzene, giving a yellow solution exhibiting a violet fluorescence, and the colourless solution in methyl alcohol also shows a beautiful violet fluorescence which instantly vanishes on the addition of a trace of acid (even acetic acid), with the formation of a yellow solution showing a light green fluorescence.

This dihydro-derivative (1·5 gms.) was melted, intimately mixed with lead oxide (12 gms.), and heated under reduced pressure. The distillate, which at once solidified, crystallised from benzene in very pale yellow, thin prisms (1 gm.), m. p. 186°, and 186—187° after recrystallisation (Found : C = 83·58; H = 4·37; N = 11·87 $C_{16}H_{10}N_2$ requires C = 83·5; H = 4·3; N = 12·2 per cent.).

2 : 3-*Quinoquinoline* is a strong base easily soluble in dilute hydrochloric acid to a yellow, non-fluorescent solution. The base dissolves, however, in concentrated sulphuric acid, giving a deep yellow solution with an intense yellowish-green fluorescence. It is easily soluble in methyl alcohol to an almost colourless solution which, unlike that of the dihydro-derivative, exhibits no trace of fluorescence.

4-*Hydroxytetrahydroquinoline* (XIX) and 4 : 4′-*Dihydroxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-4 : 4′-*diquinolyl* (XX).—To a

* An entirely different result is obtained if the water and ethyl alcohol used in the above condensation are replaced by amyl alcohol, but this reaction has not been fully investigated.

solution of 4-tetrahydroquinolone (3 gms.) in alcohol (15 c.c.) at 55°, sodium amalgam (22 gms. of 4 per cent.) was added in four portions with vigorous shaking. A rise of temperature occurred, the yellow fluorescence of the solution faded, and a colourless solid (1 gm.) soon began to separate.

After some minutes, water was added, the colourless precipitate collected, washed with a little hot water (filtrate A), and crystallised from pyridine, from which the pinacol separated in thin, colourless prisms, decomposing at 235° and giving a clear melt at 260° (Found : C = 72·6; H = 6·6. $C_{18}H_{20}O_2N_2$ requires C = 73·0; H = 6·7 per cent.).

This pinacol (XX) is almost insoluble in alcohol or benzene, but readily soluble in dilute mineral acids giving colourless solutions. It dissolves in concentrated sulphuric acid to a purple solution which quickly changes to light red and then becomes almost colourless.

The cloudy filtrate (A) was shaken with a little ether and the aqueous layer evaporated almost to dryness on the steam-bath. An oil gradually separated and, on cooling in ice-water, set to a brittle mass. This was dried in a vacuum desiccator and the viscous, brown mass extracted with a mixture of equal volumes of hot benzene and light petroleum (b. p. 100—120°), when, on standing, long, colourless, well-defined prisms (1 gm.) separated and, after recrystallisation, melted at 83—84° (Found : C = 73·0; H = 7·4; N = 9·2. $C_9H_{11}ON$ requires C = 72·5; H = 7·4; N = 9·4 per cent.).

4-*Hydroxytetrahydroquinoline* is readily soluble in warm water or the usual organic solvents and is a strong base. It dissolves in cold concentrated sulphuric acid to a pale red solution. The *diacetyl* derivative, prepared by means of boiling acetic anhydride, crystallises from light petroleum (b. p. 100—120°), in which it is more soluble than the free base, in colourless, ill-defined prisms, m. p. 95—96° (Found : C = 67·3; H = 6·6. $C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4 per cent.).

1 : 2 : 1′ : 2′-*Tetrahydro*-4 : 4′-*diquinolyl* (XXI), 1 : 2-*Dihydro*-4 : 4′-*diquinolyl* (XXII), and 4 : 4′-*Diquinolyl* (XXIII).—The pinacol (XX; 0·7 gm.) was dissolved in concentrated sulphuric acid (7 c.c.), the whole being well cooled during the addition, when the purple solution formed at first, quickly changed to light red and then to pale brown. After standing at the ordinary temperature for 10 minutes, the solution was treated with ice, and the colourless sulphate collected and decomposed by ammonia. The faintly yellow solid (0·5 gm.) obtained separated from methyl alcohol in pale lemon, well-defined bi-pyramids which softened at 155° and

melted at 165° (Found: C = 83·0; H = 6·3; N = 10·4. $C_{18}H_{16}N_2$ requires C = 83·1; H = 6·1; N = 10·8 per cent.). The base (XXI) gives violet fluorescent solutions in alcohol or benzene, but a colourless solution in concentrated sulphuric acid which slowly changes to pink and develops a deep violet fluorescence. It is converted, on boiling with acetic anhydride, into the *diacetyl* derivative which separates from alcohol in stout, colourless prisms, m. p. 230—231° (Found: C = 77·2; H = 5·7. $C_{22}H_{20}O_2N_2$ requires C = 76·7; H = 5·8 per cent.).

On boiling a methyl alcoholic solution of the base (XXI) for 2 hours, partial oxidation occurs and, on standing, a light yellow, rather ill-defined, crystalline deposit of the dihydro-derivative (XXII) is obtained which, after crystallising from methyl alcohol, softens at 200° and melts at 210° (Found: C = 83·9; H = 5·4. $C_{18}H_{14}N_2$ requires C = 83·7; H = 5·4 per cent.). When this dihydro-derivative, suspended in methyl alcohol, is left exposed to the air, dissolution gradually occurs and, after a week, the addition of water precipitates 4 : 4′-*diquinolyl* (XXIII), which crystallises from light petroleum in almost colourless, thin prisms, m. p. 166° (Found: C = 84·5; H = 4·8. $C_{18}H_{12}N_2$ requires C = 84·4; H = 4·7 per cent.).

4 : 4′-Diquinolyl is a strong base readily soluble in dilute mineral acids and also in alcohol or benzene.

The authors are indebted to the British Dyestuffs Corporation for permission to publish the results of this investigation.

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CCXIII.—*Condensation of Aryldiazonium Salts and of Alkyl Nitrites with certain Derivatives of Cyanoacetic Acid.*

By THOMAS KENNEDY WALKER.

IN extension of the investigation dealing with the action of aryldiazonium salts on monoalkylmalonic acids (J., 1923, **123**, 2775) a study has been made of the action of these salts on monoalkylcyanoacetic acids, and of the behaviour of nitrous acid and alkyl nitrites towards the latter acids and their esters.

When solutions of aryldiazonium salts were allowed to react with alkylcyanoacetic acids, carbon dioxide was liberated and hydrazones (type I) were produced:

$$1.\ CHR(CO_2H)\cdot CN + Ar\cdot N_2\cdot OH \longrightarrow CR(:N\cdot NHAr)\cdot CN + CO_2 + H_2O.$$

(R = CH_2Ph, Ph, or Et.)

On the other hand, nitrous acid and alkyl nitrites were without action on monoalkylcyanoacetic acids, whilst the esters of these acids also resisted attack to a large extent and only under one set of conditions could be made to yield oximino-derivatives, $CR(:N\cdot OH)\cdot CN$ (type II). The reason for this lack of activity is not evident, for it has long been known that nitrous acid condenses with the monoalkylated malonic acids and their esters.

Based on the results obtained now and previously (*loc. cit.*), the following generalisation may be advanced: An aryldiazonium salt condenses with a compound of the type CHRXY, where X = CO_2H, CO_2R', COR', CN, and Y = CO_2H, CO_2R' (R and R' being alkyl groups); whilst an alkyl nitrite condenses with such a compound in all cases except those in which, at the same time, X = CN and Y = CO_2H.

It was deemed of interest to investigate the action of nitrosobenzene on methine compounds of the same type (CHRXY) in view of the well-known tendency of the nitroso-group to react with substances containing positively polarised hydrogen. In no case, however, could interaction be brought about, although, for the most part, condensation readily occurred with the corresponding methylene derivatives (CH_2XY).*

Experimental.

The difficulties experienced by Cassirer (*Ber.*, 1892, **25**, 3028) and Hessler (*Amer. Chem. J.*, 1899, **22**, 169) in monobenzylating cyanoacetic ester can be largely overcome by the use of an excess of the ester (3 mols. to 1 of benzyl chloride and 1 of sodium ethoxide). The yield is 60 per cent. of the theoretical, the production of the dibenzyl compound being negligible, and the excess of ethyl cyanoacetate can be recovered by distillation. The benzyl-ester can be converted into the benzyl-acid by shaking for 10 minutes with the necessary quantity of 20 per cent. sodium hydroxide and neutralising with cold concentrated hydrochloric acid.

Phenylpyruvonitrilephenylhydrazone (This substance and the other phenylhydrazones described below belong to type I).—A diazotised solution of aniline (3·1 gms.) in hydrochloric acid (10 c.c.) was treated with sufficient sodium acetate to remove the free mineral

* Thus, ethyl malonate and nitrosobenzene yielded *ethyl phenyliminomalonate*, colourless needles, m. p. 113·5° (Found: C = 62·9; H = 6·1; N = 5·7. $C_{13}H_{15}O_4N$ requires C = 62·6; H = 6·0; N = 5·6 per cent.).

acid, and with an ice-cold solution, also containing sodium acetate, of benzylcyanoacetic acid (5·8 gms.) in 30 c.c. of water, carbon dioxide being evolved. The yellow syrup obtained solidified after remaining for 24 hours at 0°, and crystallised from warm alcohol in minute, buff plates, and from acetone in compact, star-like aggregates, m. p. 157°. Yield almost quantitative (Found: C = 76·3; H = 5·7; N = 18·1. $C_{15}H_{13}N_3$ requires C = 76·6; H = 5·5; N = 17·9 per cent.). Boiling 15 per cent. alcoholic potash converted it, with evolution of ammonia, into phenylpyruvic acid phenylhydrazone, m. p. 161°.

Phenylpyruvonitrile-p-*tolylhydrazone.*—A solution of benzylcyanoacetic acid (3·5 gms.) in an ice-cold mixture of 20 c.c. of water and 10 c.c. of alcohol was poured into a concentrated aqueous solution of *p*-toluenediazonium sulphate (1 mol.) and maintained at 0°; finally a slight excess of sodium acetate was added. The product collected after 3 hours crystallised from boiling alcohol in slender, pale yellow prisms, m. p. 113° (decomp.) (yield 25 per cent.) or from acetone or light petroleum (Found: C = 76·8; H = 6·3; N = 17·0. $C_{16}H_{15}N_3$ requires C = 77·1; H = 6·0; N = 16·9 per cent.).

Phenylpyruvonitrile-p-*nitrophenylhydrazone*, obtained in small yield when a solution of diazotised *p*-nitroaniline was mixed with an aqueous solution of the sodium salt of benzylcyanoacetic acid, crystallised from chloroform in deep yellow, microscopic prisms, m. p. 167—168°, with frothing (Found: N = 20·2. $C_{15}H_{12}O_2N_4$ requires N = 20·0 per cent.).

Methylpyruvonitrile-p-*tolylhydrazone*, prepared in the same way as the corresponding derivative of phenylpyruvonitrile, melts at 143—144° (compare Favrel, *Compt. rend.*, 1901, **132**, 983).

Methylpyruvonitrile-p-*chlorophenylhydrazone* was prepared in almost quantitative yield by the same general method. It was found advantageous to carry out the diazotisation of the *p*-chloroaniline and the subsequent condensation in presence of glacial acetic acid. The substance is very sparingly soluble in the usual organic solvents. After successive crystallisations from hot glacial acetic acid and boiling benzene, it formed minute, crimson leaflets, m. p. 172° (Found: N = 20·4. $C_{10}H_{10}N_3Cl$ requires N = 20·29 per cent.).

Phenylglyoxylonitrilephenylhydrazone.—A solution of the sodium salt of ethyl phenylcyanoacetate in a small volume of ice-water was treated with a concentrated aqueous solution of crystalline benzenediazonium sulphate (1 mol.), followed by potassium carbonate (1 mol.). Recrystallised from hot glacial acetic acid and from hot acetone, the product formed sulphur-yellow needles, m. p. 152° (compare Sachs and Bry, *Ber.*, 1901, **34**, 118).

Phenylpyruvonitrile Oxime (Type II).—Solutions of ethyl benzylcyanoacetate (4 gms.) and amyl nitrite (2·35 gms.) in 60 c.c. of dry ether and of potassium ethoxide (1 mol.) in absolute ether (Hantzsch and Lehmann, *Ber.*, 1901, **34**, 2512) were mixed at 0° and kept cold. After 48 hours, the crystalline product was washed with dry ether, when it became almost colourless; it was extremely hygroscopic, changing in the air to a dark, sticky mass. On cautious acidification, the free oxime separated as a red oil, which could not be induced to crystallise and was unstable. The *silver* salt was obtained from the potassium salt as a white, amorphous powder which slowly darkened in daylight (Found: Ag = 40·7. $C_9H_7ON_2Ag$ requires Ag = 40·42 per cent.). The constitution of the oxime was proved by the facts that on boiling with hydrochloric acid and subsequent basification it gave hydroxylamine, whilst on heating with an excess of 15 per cent. alcoholic potash for 4 hours, followed by acidification, it yielded α-oximino-β-phenylpropionic acid, m. p. 159—160°.

Methylpyruvonitrile oxime (type II), a red oil, was obtained in the form of its potassium salt by the interaction of ethyl ethylcyanoacetate and amyl nitrite or ethyl nitrite as in the previous preparation. The salts with sodium and potassium are extremely hygroscopic, the *silver* salt is a yellowish-white powder which darkens in daylight (Found: Ag = 52·4. $C_4H_5ON_2Ag$ requires Ag = 52·65 per cent.). Attempts to prepare derivatives of this oxime resulted only in its decomposition.

Phenylglyoxylonitrile oxime (type II) was prepared in small quantity from ethyl phenylcyanoacetate by the new method, which in this case was modified in that a larger proportion of absolute alcohol was used to keep in solution ethyl phenylsodiocyanoacetate. This oxime separated from hot water in plates, m. p. 129° (compare A. Meyer, *Ber.*, 1898, **21**, 1314; Sachs, *ibid.*, 1900, **33**, 963).

The above experiments form part of a scheme of work which was undertaken at the suggestion of Professor A. Lapworth, F.R.S., to whom the author is greatly indebted for numerous helpful suggestions. Acknowledgment is also gratefully made to the Advisory Council of the Department of Scientific and Industrial Research for a grant which facilitated the work.

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CCXIV.—*The Behaviour of Titanic Acid towards Hydrochloric Acid.*

By Arthur Milnes Morley and John Kerfoot Wood.

Collins and Wood (J., 1922, **121**, 441) have recently advanced the hypothesis that the existence of different modifications of stannic acid and the gradual conversion of one variety into another which takes place under certain conditions may be traced to the amphoteric nature of stannic hydroxide, which makes it possible for salt-like condensation products to be formed. It has been shown that the behaviour of the modifications of stannic acid is in accordance with this view, and it was also suggested that the same hypothesis might be applied in connexion with the analogous compounds of titanium: the present communication gives an account of experiments which have been made to test this matter.

A reference to the literature at once shows a certain amount of evidence in support of the suggestion advanced by Collins and Wood. Titanic hydroxide is undoubtedly possessed of an amphoteric character, although, in view of its slight solubility in alkaline hydroxides, it would appear that the acidic tendency of the substance is not very pronounced. It would therefore be quite possible for condensation between molecules of the substance, functioning respectively as acid and base, to occur, thus leading to the production of molecules of greater complexity. The observations of Rose (*Pogg. Ann.*, 1844, **61**, 507), Merz (*J. pr. Chem.*, 1866, **99**, 157), Demoly (*Compt. Chim.*, 1849, 325), and Weber (*Pogg. Ann.*, 1863, **120**, 287) show clearly that the properties of titanic hydroxide are influenced by the conditions under which it is prepared; when the whole of the operations involved in the preparation are conducted at the ordinary temperature, the substance obtained is readily soluble in dilute mineral acids, whereas the substance precipitated from a boiling solution is insoluble in solutions of acids; moreover, a product precipitated in the cold becomes less and less soluble in dilute acids if left for a long period in contact with cold water, washed with hot water, or dried at temperatures of 100° and upwards, the change of properties evidently being due to the transformation of the α-modification into the β-variety. It would also appear that the α—β change is capable of reversal, inasmuch as β-titanic acid may be brought into solution by prolonged heating with concentrated sulphuric acid.

The experiments made by the authors have involved the determination of the amount of titanium passing into colloidal solution, as well as that passing into true solution, when different varieties

of titanic acid have been subjected to the action of hydrochloric acid. The results show that in every aspect of the question the behaviour of the titanium compounds is in agreement with the requirements of the theory advanced by Collins and Wood. It may also be mentioned that the behaviour of different modifications of titanic acid towards dyestuffs (*J. Soc. Dyers & Col.*, 1923, **39**, 100) furnishes additional evidence in support of the hypothesis.

Experimental.

All the samples of titanic acid employed were prepared from titanic chloride by treatment with ammonia, as already described in detail in another paper (*J. Soc. Dyers & Col., loc. cit.*); the characteristics of the various samples are shown in Table I.

Table I.

	Sample.			
	A.	B.	C.	D.
Modification of acid	α	α	β	β
Colour	White.	Pale cream.	Buff.	Deep cream.
Mode of drying	In air.	In vac. over H_2SO_4.	In air at 75—85°.	In air.
Percentage of H_2O	33·80	13·82	13·53	23·88
Percentage of NH_3	2·50	2·73	0·19	trace
Percentage of Cl	trace	trace	trace	0·35

The difference in the purity of the samples is easily accounted for on the hypothesis of Collins and Wood, for with the α-variety, prepared at about 25°, much more adsorption of base is possible than with the more condensed β-modification prepared at 100°.

The general method of investigation employed was to add an excess of the solid to solutions of hydrochloric acid of varying concentration prepared by the dilution of the pure redistilled acid. The mixtures were contained in flasks closed by waxed corks, and were kept in a thermostat maintained at 25°. From time to time the contents of the flasks were examined and analysed; great care was necessary to avoid disturbing the precipitate when pipetting off the solution for analysis because of the very finely divided condition of the former and the extreme difficulty of separating the suspended particles by the process of filtration. The composition of both the supernatant liquid and of the ultra-filtrate obtained by the use of collodion membranes was determined; the membranes were prepared by the method described by Collins and Wood (J., 1922, **121**, 1130), 50 c.c. of collodion solution being used for the preparation of each of the films.

The acidity of the solution was determined by titration with sodium hydroxide, using methyl-orange as indicator. When

phenolphthalein was employed as indicator, slightly larger volumes of alkali were required than with methyl-orange, the difference being the greater the larger the amount of titanium in the solution; this would suggest that the precipitated titanic acid is capable of affecting phenolphthalein. The quantity of titanium in the solutions was estimated by treating the acid liquid with aluminium and titrating with a standard solution of iron alum under the conditions described in a recent paper (this vol., p. 518).

Experiments with Sample A.—After carrying out a number of preliminary experiments a series of experiments involving five solutions of hydrochloric acid was commenced, the concentration of the acid ranging approximately from 0·1*N* to 0·9*N*. The behaviour of the titanic acid under the influence of the acid solution was kept under constant observation and the changes noticed may be summarised as follows:

(*a*) A yellow solid was deposited from the solutions in flasks 77, 78, 79, 80 at the ordinary temperature, and a much larger amount of a solid of similar appearance was precipitated as soon as the temperature of the solutions was raised to 25°.

(*b*) The solid in flask 77 was obviously peptising slowly until finally a distinctly colloidal solution was produced.

(*c*) The solids in flasks 78 and 79 appeared to peptise, but were afterwards deposited from solution.

(*d*) No peptisation appeared to take place in flasks 80 and 81. Some of the analytical results obtained are given in Table II, the concentration of titanium dioxide being expressed in millimols. per litre and that of hydrochloric acid in normalities.

TABLE II.

	Before ultra-filtration.			After ultra-filtration.		
Flask.	Days from start.	TiO_2.	HCl.	Days from start.	TiO_2.	HCl.
77	54	3·73	0·103	46	0·80	0·105
	127	5·50	0·106	119	0·14	0·110
	182	5·94	0·105			
78	54	0·92	0·260	46	1·37	0·263
	127	0·65	0·261	124	0·49	0·264
	182	0·57	0·261			
79	54	4·39	0·527	51	4·63	0·532
	127	2·59	0·527	124	2·57	0·542
	181	1·46	0·532			
80	54	7·20	0·715	49	7·26	0·729
	127	5·92	0·713	124	5·95	0·720
	181	3·73	0·715			
81	54	19·09	0·883	47	23·21	0·927
	127	4·45	0·884	131	3·51	0·897
	181	1·97	0·882			

Experiments with Sample B.—Generally speaking, the behaviour observed when this preparation was treated with hydrochloric acid

was of a similar character to that observed with sample A, a yellow solid being deposited from the various mixtures after they had stood for some time; no peptisation was observed to take place in the solutions of hydrochloric acid ranging from 0·7*N* to 2·2*N*. The analytical results obtained from the supernatant liquids and the ultra-filtrates are given in Table III.

TABLE III.

	Before ultra-filtration.			After ultra-filtration.		
Flask.	Days from start.	TiO_2.	HCl.	Days from start.	TiO_2.	HCl.
85	37	9·67	0·102	38	2·69	0·104
	106	11·24	0·106	107	0·18	0·116
	157	11·35	0·108			
86	37	1·36	0·224	38	1·58	0·230
	106	1·27	0·228	109	0·47	0·231
	157	0·87	0·228			
87	37	5·16	0·498	44	4·98	0·508
	105	2·07	0·503	109	1·56	0·502
	157	1·23	0·502			
88	37	8·53	0·704	44	8·70	0·723
	105	5·39	0·707			
	157	3·31	0·708			
89	37	11·65	0·909	44	12·21	0·925
	105	10·23	0·909	109	9·89	0·904
	157	7·23	0·912			
90	37	19·30	1·378	45	19·63	1·380
	105	14·67	1·379	113	14·35	1·451
	157	10·49	1·383			
91	37	31·58	1·828	45	37·99	1·847
	106	39·52	1·834			
	156	30·67	1·835			
92	37	53·70	2·216	45	52·47	2·205
	106	62·92	2·218	113	62·97	2·230
	157	57·90	2·218			

Experiments with Sample C.—In this series of experiments the hydrochloric acid used varied in concentration between 0·265*N* and 1·503*N*. In the most dilute acid an extremely colloidal solution appeared to have formed after 15 days, but coagulation then commenced, leaving ultimately a solution which was only faintly opalescent. Slight peptisation was observed in the case of acid having a concentration of from 0·5*N* to 0·7*N*, but no signs of peptisation could be seen in the case of more concentrated solutions of acid. As already mentioned, this sample of titanic acid had a distinct buff colour, but it was observed that the surface layer of the titanic acid in the flasks was practically white, whilst that at the bottom of the flasks appeared to be darker in colour than the original substance. It would appear probable that the colour is dependent on the degree of subdivision, the more finely divided particles being white. The results obtained by the analysis of the liquids are given in Table IV.

TABLE IV.

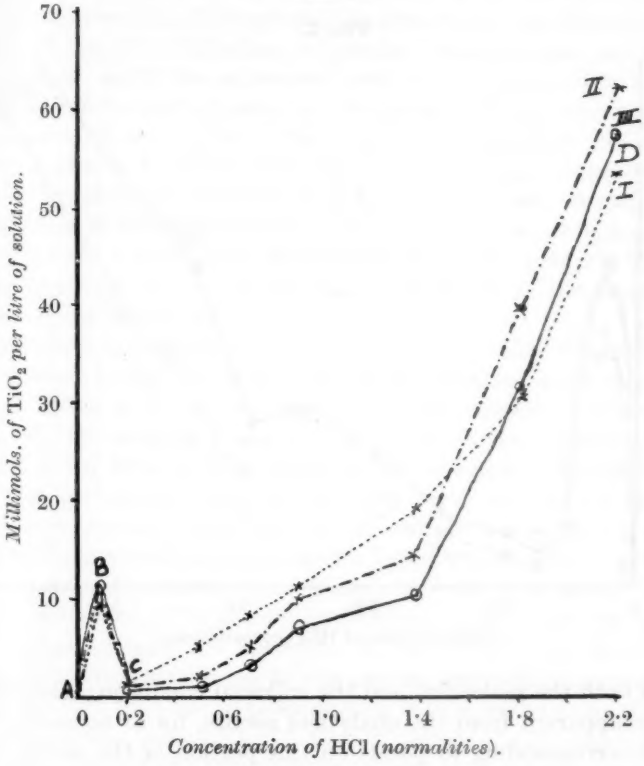
	Before ultra-filtration.			After ultra-filtration.		
Flask.	Days from start.	TiO_2.	HCl.	Days from start.	TiO_2.	HCl.
66	71	0·19	0·265			
	138	0·40	0·262	116	nil	0·264
	188	0·47	0·261	187	0·15	0·271
66*a*	54	0·34	0·500			
	121	0·90	0·500	99	0·23	0·497
	171	1·28	0·502	170	0·48	0·505
67	71	0·52	0·715			
	138	0·95	0·720	116	0·33	0·718
	188	1·12	0·715	188	0·71	0·732
68	71	0·43	1·017			
	138	0·92	1·023	117	0·45	1·034
	188	1·78	1·025			
69	71	0·77	1·503			
	138	1·50	1·505	117	0·94	1·508
	188	1·96	1·507	188	1·77	1·537

TABLE V.

	Before ultra-filtration.			After ultra-filtration.		
Flask.	Days from start.	TiO_2.	HCl.	Days from start.	TiO_2.	HCl.
53	56	6·56	0·245			
	98	5·97	0·248	96	nil	0·252
	154	8·18	0·249	167	nil	0·253
54	91	7·79	0·525			
	133	7·00	0·519	131	nil	0·531
	189	9·41	0·525	202	0·28	0·547
55	56	5·77	0·751			
	99	5·71	0·751	97	0·31	0·761
	154	7·14	0·756			
56	91	1·91	1·035			
	134	1·90	1·028	132	0·39	1·102
	191	2·48	1·037	202	0·71	1·056
58	56	0·42	1·475			
	99	0·50	1·475	97	0·16	1·473
	155	0·90	1·471	168	0·74	1·564
59	91	0·95	1·960			
	134	1·01	1·958	141	1·00	2·016
	191	1·59	1·962			
60	91	1·17	2·935			
	134	1·60	2·935	141	1·63	2·975
	191	2·25	2·936	203	2·44	3·022
61	91	2·25	3·936			
	134	2·90	3·931	141	2·36	3·919
	191	4·17	3·937			
62	91	2·56	5·175			
	134	3·50	5·163	160	4·16	5·083
	191	5·44	5·157	203	7·02	5·177
63	92	2·36	5·910			
	134	3·31	5·903	160	4·13	6·016
	192	5·11	5·900			
64	92	4·54	6·768			
	134	5·56	6·760	160	7·02	6·515
	192	9·62	6·749			
65	92	14·81	9·871			
	134	14·68	9·838			
	192	17·53	9·807			

Experiments with Sample D.—The acid employed in this series of experiments varied in concentration between 0·25*N* and pure concentrated acid. In those mixtures where a concentration of 0·75*N* was not exceeded, the titanic acid gradually peptised with the formation of true colloidal solutions; with *N*-hydrochloric acid, the titanic acid appeared to undergo peptisation, but the solution obtained was found to be perfectly clear. No signs of peptisation were observed with the more concentrated solutions. The analytical results of the mixtures are shown in Table V.

FIG. 1.



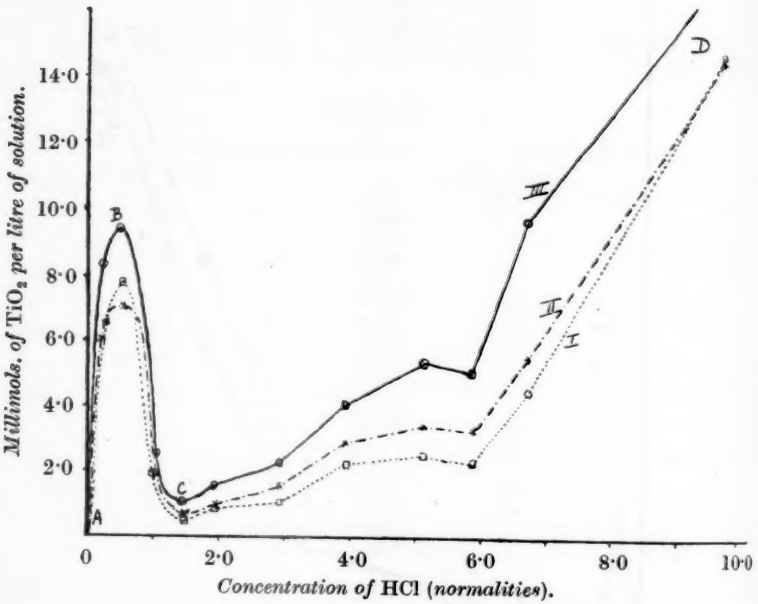
Discussion of Results.

The influence of time and increasing concentration of hydrochloric acid on the total amount of titanium in the liquids is readily seen from the curves shown in Figs. 1 and 2, which show the analytical results before ultra-filtration of the liquids prepared from samples B and D respectively. These curves may be taken as representative of the behaviour towards hydrochloric acid of α-titanic acid and

β-titanic acid respectively. The increasing age of the systems is indicated by the higher number attached to the curve.

It will be apparent that in both cases the "solubility" curves may be regarded as made up of two portions, namely the first portion *ABC* in which, with increasing concentration of acid, the titanium content rises to a maximum *B* and then falls to *C*, and the second portion *CD* where, with still higher concentrations of hydrochloric acid, the amount of titanium steadily increases as the concentration of the acid is increased. The portion *ABC* of the curve corresponds with the simultaneous presence in the liquid of titanic

FIG. 2.



acid in both the molecular and the colloidal condition; this will at once be apparent from the analytical results, for at concentrations of acid corresponding to points on this portion of the curves there was always considerably more titanium in the solution before ultra-filtration than was present after ultra-filtration. With concentrations of acid greater than that indicated by the point *C*, the amounts of titanium in the liquids before and after ultra-filtration were practically identical, so that the portion *CD* of the curves indicates the presence only of titanic acid in a state of true solution. It will be observed that the point beyond which titanic acid is no longer present in the colloidal condition differs considerably

according to the character of the sample; with α-titanic acid none of the substance is in the colloidal state when the hydrochloric acid has a concentration greater than 0·25*N*, but with the β-variety the colloidal condition persists until the hydrochloric acid has a concentration of 1·5*N*.

These results are quite in agreement with the hypothesis of Collins and Wood (*loc. cit.*) and with the conclusions drawn by them concerning the behaviour of different modifications of stannic acid and analogous compounds towards hydrochloric acid (J., 1922, **121**, 1122). In accordance with the views expressed, it would be anticipated that, because of the greater complexity and smaller adsorptive power of the β-modification, a greater concentration of hydrochloric acid would be necessary both for its peptisation and for bringing it into true solution as compared with the concentration necessary with the α-acid. The shape of the portion *ABC* of the curves is also in harmony with the views previously expressed, for after a certain degree of peptisation has been reached, corresponding to the point *B*, further increase in the concentration of hydrochloric acid will have a salting-out effect and will lead to a steady decrease in the titanium content of the liquid, as shown in the descending portion *BC* of the curves.

The influence exerted by the mode of preparation of titanic acid with respect to its behaviour towards hydrochloric acid of a given concentration is well illustrated by a comparison of the results obtained with samples C and D. Whilst both these products were thrown down from boiling solutions of titanium tetrachloride so that the precipitate obtained in each case would possess the β-character, the fact that the former sample was dried at a considerably higher temperature than the latter would cause it to be in a more condensed condition than sample D; this is indicated by the greater resistance to attack by hydrochloric acid shown by sample C as compared with the behaviour of sample D. Another factor which probably contributed to the greater susceptibility of sample D was the fact that in the precipitation of this variety the addition of ammonia was stopped while the solution was still slightly acid, whereas in the case of all the other specimens the ammonia was added until the liquid was distinctly alkaline. Sample D would therefore tend to carry a positive electrical charge, whilst the other specimens would be negatively charged and therefore would not be in a condition to be so readily peptised when introduced into hydrochloric acid. The difference in the amounts of samples A and B peptised by hydrochloric acid of the same concentration is also due to a difference in their respective degrees of condensation arising from the different methods of drying employed. For the adsorption of a

given amount of hydrochloric acid, a larger quantity of the more condensed variety B would be required than of the less condensed sample A.

As regards the influence of time on the composition of the liquids obtained, it is obvious that, just as with stannic acid, so also with titanic acid, a condition of equilibrium between the solution and the undissolved substance is only attained very slowly. As a general conclusion it may be stated that, as the liquids become of increasing age, the content of titanium in the mixtures prepared from the α-acid shows a continual decrease, whilst with the mixtures obtained from the β-acid the change is in the reverse direction. These results are readily understood when it is remembered that two opposed actions may take place in systems composed of titanic acid and hydrochloric acid, namely, (*a*) condensation of the molecules with the formation of more complex particles, and (*b*) disintegration of the original particles of titanic acid with the production of simpler ones which are capable of being more readily peptised and dissolved. Either of these changes will bring about a disturbance of equilibrium, but the disturbance will be in opposite directions in the two cases. In those systems containing the α-acid the progress of the α—β change will lead to a continual falling off in the titanium content of the liquid, whilst in systems prepared from the β-acid the hydrochloric acid will tend to have a disruptive effect, thus bringing about the reversal of the α—β change and the steady increase, with increasing time, of the amount of titanium in the liquid.

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CCXV.—*The Explosion of Acetylene and Nitrogen. Part III. The Effect of the Addition of Oxygen on the Production of Hydrocyanic Acid.*

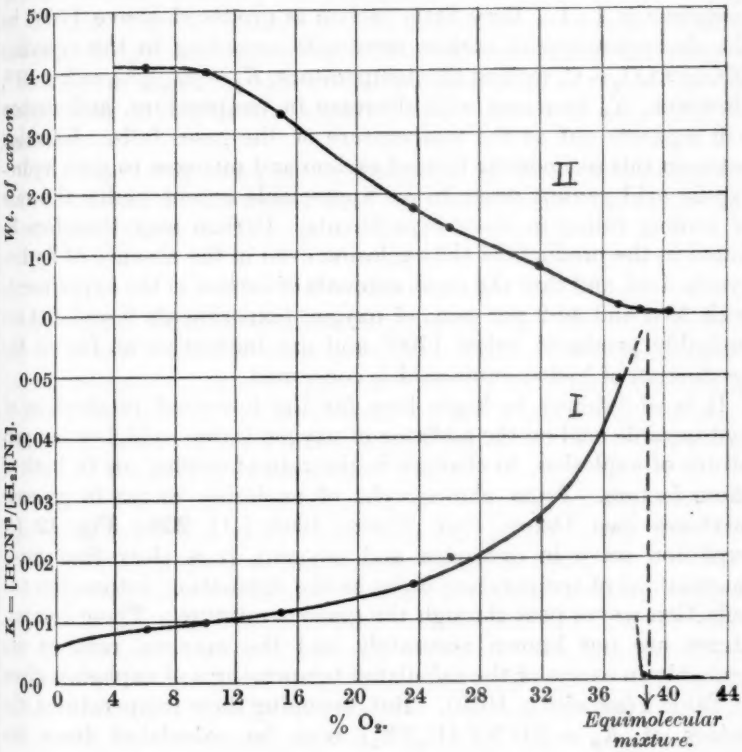
By WILLIAM EDWARD GARNER and SIDNEY WALTER SAUNDERS.

IN previous papers (J., 1921, **119**, 1903; 1922, **121**, 1729), it was shown that hydrocyanic acid is produced in explosions of mixtures of acetylene and nitrogen, in amounts given by the relation $[HCN] = K_1^{II}[C][N_2]^{0·37}$ where $K_1^{II} = 0·079$. Further experiments, carried out with mixtures of oxygen, nitrogen, and acetylene, have shown that this relationship does not hold when oxygen is present.

In the series of experiments recorded below, the nitrogen in the gaseous mixture was maintained practically constant at 21 to 23 per cent. and the ratio of acetylene to oxygen varied between wide

limits. The total initial pressure was about 3 atmospheres in every case. The more important data obtained are collected together in Tables III and IV, and in Fig. 1. From these tables, it will be seen that the concentration of hydrocyanic acid and the values of K and K_1^{II} increase as the percentage of oxygen rises. The rate of increase is slow at first and then more rapid as the ratio of oxygen to acetylene approaches that of the equimolecular mixture. When oxygen is in

FIG. 1.



excess of the 1 : 1 ratio, the concentration of hydrocyanic acid and also K_1^{II} and K fall abruptly to zero (see curve I, where K is plotted against the percentage of oxygen). The sudden decrease in the yield of hydrocyanic acid coincides with the disappearance of carbon from the products (see curve II).

The explosion of mixtures of oxygen, nitrogen, and acetylene may be expected to give rise to hydrocyanic acid only if free carbon be present in the products at temperatures above about 1700°.*

* The chilling temperature for the reaction giving hydrocyanic acid. Below this temperature, the reaction is extremely slow (*v.* Wartenberg).

If acetylene is in excess, since there are only two principal primary reactions in the detonation wave (Dixon),

(1) $C_2H_2 \rightleftharpoons 2C + H_2 + 54{,}880$ cals. at const. vol. at 20°.

(2) $C_2H_2 + O_2 \longrightarrow 2CO + H_2 + 108{,}130$ „ „ „

carbon will be present at the highest temperatures of the explosion, and hydrocyanic acid will be formed. That this is the true mechanism of the reactions occurring in the explosion wave is confirmed by the break in curve I occurring when the ratio of oxygen to acetylene is 1 : 1. Very little carbon is produced above 1700° by the decomposition of carbon monoxide according to the equation $2CO \rightleftharpoons CO_2 + C$, since at this temperature, $K_p = p_{CO_2}/p^2_{CO} = 2 \times 10^{-5}$. However, K_p increases with decrease in temperature, and carbon will separate out as the temperature of the gases falls. Reaction between this secondarily formed carbon and nitrogen to give hydrocyanic acid cannot occur to an appreciable extent under the rate of cooling ruling in these experiments. Carbon may therefore be found in the products of the explosion even in the absence of hydrocyanic acid, and thus the small amounts of carbon in the experiments with 38·5 and 40·2 per cent. of oxygen (experiments 9 and 14) are probably produced below 1700° and are ineffective as far as the production of hydrocyanic acid is concerned.

It is of interest to know how far the increased production of hydrocyanic acid on the addition of oxygen is due to higher temperatures of explosion, to changes in the rate of cooling, or to both of these factors. From photographs of explosion waves in gaseous mixtures (see Dixon, *Phil. Trans.*, 1903, [*A*], **200**; Fig. 12 for explosion wave in cyanogen and oxygen), it is clear that rapid fluctuations of temperature occur as the detonation, retonation and reflection waves pass through the gaseous mixture. These temperatures are not known accurately and the maxima reached are probably in excess of the calculated temperatures of explosion given in Table I (see also p. 1639). But, assuming these temperatures, the values of $K_p = [HCN]^2/[H_2][N_2]$ may be calculated from the equation

$$\log K_p = -13{,}210/T + 0{\cdot}625 \log T - 0{\cdot}0009515\, T + 1{\cdot}18 \times 10^{-7} T^2 + 3{\cdot}4.$$

These are much higher than the experimental values (Table I), although they increase in the same manner as the oxygen percentage rises (bottom two lines) :

TABLE I.

% O_2	0	10·03	23·68	31·88	37·01
$T°$	2795	3088	3595	3982	4287
K calc.	0·32	0·31	1·12	2·61	4·03
K found	0·0069	0·0101	0·0164	0·0263	0·0497

It is thus clear that the composition of the final gaseous mixture will depend not only on the composition in the explosion and reflection waves, but also on the rate of cooling. The cooling at these high temperatures is almost entirely due to loss of heat by chemical and thermal radiation, and to this radiation the gaseous products are themselves almost transparent. Hence, if the products are completely gaseous, cooling will take place comparatively rapidly. On the other hand, carbon is an almost perfect black body, and its presence in any quantity will materially reduce the rate of cooling. It therefore follows that the rate of cooling becomes more rapid as the percentage of oxygen rises. Thus the increase in the yield of hydrocyanic acid may be attributed partly to increases in the temperature of explosion and partly to a more rapid cooling of the products.

The carbon may also play the part of a catalyst, accelerating the decomposition of hydrocyanic acid into its elements, and this action would be in the same direction.

Experimental.

Apparatus.—A spherical phosphor-bronze bomb with walls about one half-inch thick and internal volume 2048 c.c. was used during this investigation. It held a vacuum for 24 hours without appreciable leakage, and owing to the increase in the thickness of the walls there was no leak of gases during the explosion, a difficulty met with in some of the earlier experiments.

The small *J* manometer (*loc. cit.*, p. 1907) was recalibrated, the agreement with the older calibration being within 0·2 per cent. The remaining apparatus has already been described.

Analysis of Gases.—The acetylene in mixtures of nitrogen, oxygen, and acetylene was determined by combustion over copper oxide and absorption of the carbon dioxide produced. A measured volume of the mixture was diluted with air, freed from organic matter and carbon dioxide, so as to give a mixture containing about 1 per cent. of acetylene. This mixture was then burnt over heated copper oxide and the carbon dioxide produced was absorbed in two bubblers containing baryta solution and fitted with mercury-sealed stirrers rotating at about 800 r.p.m. Bulb and Gahl type bubblers were found to be unsatisfactory for this analysis, even with the rate of passage of the gas as low as $\frac{1}{2}$ litre per hour. The nitrogen was determined after removal of the acetylene and oxygen by solutions of ammoniacal cuprous chloride and alkaline pyrogallol in the apparatus described by one of us (J., 1923, **123**, 2826). The oxygen was obtained by difference. These measurements were checked against the manometric readings made during the mixing of the gases.

Complete analyses of some of the final gaseous mixtures were made by the ordinary methods (Table III). Hydrocyanic acid and ammonia were determined by the methods described previously, and determinations of nitrous gases were made. In all experiments, the deposit of carbon was removed and weighed.

Results.

Series 1.—The explosion vessel was smaller than that used in the earlier experiments, and it was necessary to test if the change affected the yield of hydrocyanic acid in any way. Four explosions with acetylene and nitrogen were therefore carried out. The results are summarised in Table II.

TABLE II.

Explosions of Acetylene and Nitrogen.

Expt. No.	Initial press. (atms.).	Init. composn. % C_2H_2.	Init. composn. % N_2.	Final vol. (c.c.) at S.T.P.	Final composition. % HCN.	% NH_3.	% N_2.	% H_2.	Wt. of carbon (gms.).
1	2·80	88·95	11·05	8563	2·73	0·07	9·65	87·55	5·94
2	2·38	84·27	15·73	5037	2·82	0·04	14·30	82·82	4·42
3	2·89	86·90	13·10	5824	2·81	0·04	11·68	85·49	5·16
4	2·98	88·20	11·80	6275	2·81	0·10	10·35	86·71	5·72

These results give for $[HCN]/[C][N_2]^{0·37}$ the values :—
(1) 0·0788; (2) 0·0813; (3) 0·0803; (4) 0·0837.
The mean, 0·0810, is nearly the same as that obtained with the larger explosion vessel, *viz.* 0·0803.

TABLE III.

Explosions of Acetylene, Nitrogen, and Oxygen.

Volume of bomb, 2048 c.c.

Expt. No.	Initial press. (atms.).	Initial composition. % O_2.	% N_2.	% C_2H_2.	Final vol. of gases excl. H_2O.	Final composition. % HCN.	% NH_3.	% CO.	% CO_2.	% C_2H_2.	% N_2O_3 $\times 10^{-4}$.	Gms. of carbon. Expt.	Calc.
1	3·003	6·17	22·93	70·61	6783	3·36	0·075	13·78	0·70	1·59	1·8	4·17	4·11
2	2·889	6·14	22·78	70·80	6468	3·43	0·144	12·31	1·03	0·57	1·8	3·89	3·95
3	2·948	6·18	22·94	70·59	6865	3·23	0·092	14·30	0·92	1·11	1·8	4·19	4·18
5	3·054	6·24	23·18	70·30	6648	3·37	0·155	12·20	1·50	2·00	1·8	4·13	4·04
6	3·145	6·07	22·58	71·05	6714	3·22	0·060	9·96	0·80	0·22	1·8	4·03	4·31
7	3·430	14·85	20·98	63·90	7795	3·29	0·080	26·72	0·69	1·10	0·9	3·31	3·34
8	3·295	31·88	21·66	46·23	8516	3·52	0·037	50·89	0·53	0·20	3·2	0·84	0·81
9	2·993	40·20	22·11	37·41	6187	0·00					2·9	0·09	0·00
10	3·191	10·03	20·95	68·72	6780	3·48					1·3	3·995	3·982
11	3·066	26·00	23·00	50·68	7614	3·75					1·8	1·417	1·507
12	3·161	23·68	22·88	53·15	7356	3·67					1·8	1·787	1·886
13	3·083	37·01	22·52	40·16	9362	4·05					1·1	0·15	0·10
14	3·047	38·51	22·54	38·65	7974	0·00					0·9	0·12	0·007

Series II. Explosions of Nitrogen, Oxygen, and Acetylene.—The gases present in the products of the explosion of these three substances may include nitrogen, carbon monoxide, hydrogen, carbon dioxide,

TABLE IV.

	Final composition. Gram-mols. per litre.				$K=\frac{[HCN]^2}{[H_2][N_2]}$	$K_1^{II}=\frac{[HCN]}{[C][N_2]^{0\cdot37}}$	Temp. of explosn.	Chilling temp.
% O_2.	N_2.	H_2.	HCN.	NH_3.				
6·17	0·02817	0·09111	0·005023	0·00011	0·00983	0·1109	2959°	1952°
6·14	0·02686	0·08790	0·00484	0·00020	0·00992	0·1166	2941	1952
6·18	0·02771	0·08948	0·00484	0·00014	0·00945	0·1069	2948	1947
6·24	0·02927	0·09226	0·004883	0·00023	0·00883	0·1072	2959	1942
6·07	0·02932	0·09640	0·004710	0·00006	0·00786	0·1062	2934	1907
10·03	0·02728	0·09530	0·005122	0·00002	0·01019	0·1195	3088	1952
14·85	0·02927	0·09497	0·0055	0·00013	0·0112	0·1511	3241	1967
23·68	0·02932	0·07213	0·005888	0·00004	0·0164	0·2988	3595	2027
26·00	0·02838	0·06627	0·006212	0·00007	0·0205	0·4025	3682	2072
31·88	0·02837	0·06451	0·006934	0·00007	0·0263	0·7553	3982	2132
37·01	0·02687	0·05117	0·008262	0·00004	0·0497	5·160	4287	2282
38·51	0·03067	0·05259	0·000043	0·00004				
40·20	0·02954	0·04995	0·0	0·00003				

acetylene, hydrocyanic acid, and ammonia. Analyses of the products of explosion are included in Tables III and IV. The nitrogen content of the initial gases was maintained approximately constant between 21 and 23 per cent., since it was found in the earlier experiments that a change in the percentage of nitrogen in this region had no effect on the yield of hydrocyanic acid. The oxygen, the amount of which varied from 6 to 40 per cent., was obtained by heating pure potassium permanganate and drying over phosphoric oxide. Dry air was employed as the source of nitrogen in all the experiments, so that 0·2 to 0·3 per cent. of argon was present in each case. In Table III are given the initial pressure and composition, the volume of final gases (less water), the composition of the final gaseous mixture, and the weight of carbon found and that calculated from the analyses. Carbon dioxide and carbon were present in all the experiments. The volume of hydrocyanic acid in c.c. and its percentage in the final mixture increased with rise in the percentage of oxygen. Further data are given in Table IV, including the composition, expressed in gram mols. per litre, of the gases taking part in the hydrocyanic acid and ammonia equilibria, the temperature of explosion, the chilling temperature, and the value of K at the temperature of explosion. The percentages of nitrogen and hydrogen were calculated from the gas analyses. K rises from 0·009 to 0·050 and K_1^{II} from 0·11 to 5·2 as the percentage of oxygen increases from 6 to 37 per cent. The temperature of explosion has been calculated on the assumption that reactions (1) and (2) go to completion, and that no acetylene or hydrocyanic acid is produced in the first period of combustion. These are only approximate temperatures, as has been explained in the introduction. In these calculations the following equations have been

used for the mean molecular heats between 0° and $t°$ at constant volume :—

Carbon . . . . . $C_v = 2{\cdot}37 + 0{\cdot}00191t - 2{\cdot}23 \times 10^{-7}t^2$.
Hydrogen . . . . . $C_v = 4{\cdot}76 + 0{\cdot}00044t$.
Nitrogen and carbon monoxide $C_v = 4{\cdot}69 + 0{\cdot}000523t$.

The heats of reaction employed have been given.

The chilling temperatures, *i.e.*, those corresponding with the values of K given in column VI, are calculated from the Nernst heat theorem, and represent approximately the temperatures at which the hydrocyanic acid equilibrium

$$2C + H_2 + N_2 = 2HCN$$

is "frozen" during the cooling interval. It will be noted that up to 24 per cent. of oxygen these remain practically constant. Above this percentage, the chilling temperature rises rapidly. This, it is suggested, is caused by the decrease in the free carbon, which acts as an insulator, preventing loss of heat by radiation during the cooling interval, and thus slowing down the rate of cooling. With 37 per cent. of oxygen, when the carbon is almost reduced to zero, the rate of cooling is very rapid and hence the chilling temperature is high.

Activity of Carbon.—As it was possible that the activity of the carbon produced in the explosion played a part in the reaction, the behaviour of the carbon towards absorbents was determined. It was heated at about 300°/1 mm. for several hours to drive off any absorbed substances, and shaken with oxalic acid, which was titrated 48 hours afterwards. The following results were obtained:

% O_2 in init. gas	0	6	15	32
C.c. of N/10-acid ads. per 0·5 gm. of carbon	1·30	1·25	1·45	0·60

The activity was thus found to be very low, and did not vary markedly as the percentage of oxygen was increased.

Nitrous Gases.—The amounts of nitrous gases, determined colorimetrically by the Griess reagent, were very small (see Table III). Nitric oxide, formed directly from its elements in the explosion wave, will be in equilibrium with carbon according to the equation

$$2C + 2NO = 2CO + N_2,$$

since both nitrogen and carbon react with oxygen. The equilibrium constant for this reaction, $p^2_{CO} \cdot p_{N_2}/p^2_{NO}$, varies slightly in each experiment, the values 12·6 and 12·8 being obtained from experiments 8 and 7, which gave the greatest and the least amount of nitric oxide respectively. These values correspond to a mean

temperature of chilling of 4200° for this reaction, as deduced from an application of the Nernst heat theorem.

The Reaction $CO_2 + C = 2CO$.—Calculations of the equilibrium constant, p^2_{CO}/p_{CO_2}, for this reaction from experimental analyses of the final gaseous mixture for experiments 1—8 and from the initial percentage of oxygen and weight of carbon deposited in experiments 9, 13, and 14 have been made, and from them, using the Nernst heat theorem, the chilling temperature for the reaction has been deduced. The mean value of the chilling temperature thus obtained is 1030°. Rhead and Wheeler (J., 1910, **97**, 2178) found that this equilibrium was reached fairly rapidly above 1000°, but below this temperature equilibrium was only established slowly. The mean value of the chilling temperature from these experiments, 1030°, is thus in agreement with the results of Rhead and Wheeler, which were obtained under far different conditions.

Summary.

The hydrocyanic acid produced by the explosion of mixtures of nitrogen, oxygen, and acetylene has been determined for a range of concentrations of oxygen and acetylene, the nitrogen being kept constant at about 22 per cent. The yield of hydrocyanic acid from one gram-mol. of acetylene increases as the percentage of oxygen rises in the gaseous mixture. As the oxygen increases from 6 to 37 per cent., the value of $K = [HCN]^2/[H_2][N_2]$ increases from 0·009 to 0·05.

$K_1^{II} = [HCN]/[C][N_2]^{0·37}$, which was found to give a constant value in the earlier experiments with acetylene and nitrogen alone and admixed with helium or hydrogen, rises rapidly throughout the series. No hydrocyanic acid is found in the products of explosion if the ratio of oxygen to acetylene exceeds 1 : 1; with mixtures richer in oxygen, no appreciable amounts of carbon are liberated at the temperature of explosion, and hence hydrocyanic acid cannot be formed.

The causes of the variation of K are discussed and the increase in K as the percentage of oxygen rises is attributed to increases in the temperature of explosion and in the rate of cooling.

One of us (S. W. S.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant, for which he desires to express his thanks.

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CCXVI.—*The Ternary Alloy System Aluminium–Cadmium–Zinc.*

By Norman Frederick Budgen.

There is no recorded determination of any part of the thermal equilibrium diagram for the aluminium–cadmium–zinc alloys, and so far as the author is aware no investigation of the constitution has hitherto been attempted.

In 1913, Bayliss and Clark ("Métaux et Alliages," March 15th, 1914, Vol. VII., No. 5, p. 7), from the point of view of mechanical properties, examined alloys of compositions corresponding to the extreme aluminium corner of the diagram, and found that certain of these possessed properties likely to be of industrial value. Pierce ("Raw Material," 1922, p. 337) has studied aluminium–zinc alloys containing small quantities of cadmium, but mainly with a view to establish data concerning corrosion and disintegration phenomena which were supposed to be promoted by the presence of cadmium.

The Binary Systems.

1. *Aluminium–Cadmium.*—Of the three binary series which limit the ternary system aluminium–cadmium–zinc, one, the aluminium-cadmium series, constitutes an example representing supposed complete immiscibility in both liquid and solid states. The constitution of the system has been investigated by Wright (*J. Soc. Chem. Ind.*, 1892, **11**, 492; 1894, **13**, 1014) and Gwyer (*Z. anorg. Chem.*, 1908, **57**, 113), and the mechanical properties of aluminium-rich members by Schirmeister (*Rev. Mét.*, 1915, **12**, 464).

2. *Cadmium–Zinc.*—Pertaining to the constitution of the cadmium–zinc system an abundance of data is available; the investigators include Guertler, Hindrichs (*Z. anorg. Chem.*, 1907, **55**, 415), Kurnakow and Zemtzuzny, Bruni, Sandonnini and Quercigh (*ibid.*, 1910, **68**, 75), Mathewson and Scott (*Int. Z. Met.*, 1913, **5**, 17), Curry (*J. Physical Chem.*, 1909, **13**, 589), Lorenz and Plumbridge (*Z. anorg. Chem.*, 1913, **83**, 228), and Bingham (*J. Inst. Metals*, 1920, No. 2, p. 337). For the purposes of the present research the diagram of Hindrichs showing a simple eutectiferous series has been employed.

3. *Aluminium–Zinc.*—The aluminium–zinc binary series has been the subject of much research, earlier workers including Shepherd (*J. Physical Chem.*, 1905, **9**, 504), Eger (*Int. J. Met.*, 1913, **4**, 35), Rosenhain and Archbutt (*Phil. Trans.*, 1912, **212**, 315), Bauer and Vogel (*Int. J. Met.*, 1916, **8**, 101), and more recently Hanson and Gayler (*J. Inst. Metals*, 1922, No. 1, p. 267).

Experimental.

Preparation of Alloys.—Materials of the highest available purity were used, and the constituents carefully weighed on a sensitive balance. The aluminium was then melted in a graphite crucible and the zinc added in one or two large pieces, which readily dissolved. So soon as solution was complete, the cadmium was quickly added and the mixture vigorously stirred for about 1 minute. While still molten, the crucible and contents were transferred to a small, electrically heated furnace, maintained ready at the approximately correct temperature, and the thermocouple was inserted. In all cases the volume of alloy employed approximated closely to that recommended by Day and Sosman of the National Physical Laboratory as being a mass measuring about 2·5 cm. in diameter and 4·5 cm. deep, requiring a weight of from 50 gms. in aluminium-rich alloys to 100 gms. in zinc or cadmium-rich alloys.

Measurements of temperature were accomplished by means of a thermoelement of nickel and nickel–chromium wires twisted together at one end and insulated from one another along their length. Thin wires (No. 19, S.W.G.) were used and the junction was protected by clay couple sheaths of small bore, thus securing as high a degree of sensitivity as possible. The temperature of the cold junction was maintained constant (18°) by immersion in heavy oil contained in a vacuum flask. Calibration of the thermocouple was effected from time to time by determinations of the following fixed points made under the average working conditions: b. p. of water (100°); f. pts. of tin (232°), cadmium (321·5°), lead (327·4°), zinc (419·4°), and aluminium (658·7°).

The cooling-curve observations were obtained with a Cambridge Paul potentiometer and recorded in the form of inverse rate curves by means of a Rosenhain recording chronograph.

Readings of the *E.M.F.* developed in the thermocouple circuit were taken every 0·05 millivolt, and observations continued in most cases down to temperatures of about 200°. The accuracy obtainable with this apparatus is of a high order and frequent determinations of the same fixed point have shown differences not exceeding 1° or 2°. It is, of course, understood that some temperatures of phase change in almost any thermal investigation are only imperfectly indicated upon the cooling curves and can only be approximated whatever the method of measuring temperature; cases of this sort have been encountered in the present work. The rate of cooling was such that the temperature fell 1° in 3 seconds while the alloys were hot (about 650°) and 1° in 18 seconds when they were cooled down to about 200°. This slow rate of cooling was

adopted, because it is known that certain of the transformations and reactions which occur in alloys of the aluminium–zinc series are to a considerable extent suppressed by the more rapid rates of cooling, and it was anticipated that this feature would in some degree persist as the ternary field was entered. Even the rate adopted does not allow these reactions to be completed, but they occur to a sufficient extent for unmistakable signs of their existence to appear on the cooling curves. As has already been indicated, however, it has not been possible to study the alloys under conditions of complete equilibrium, because the method of microscopic examination after prolonged annealing would have unduly lengthened the investigation. The use of very slow cooling and the

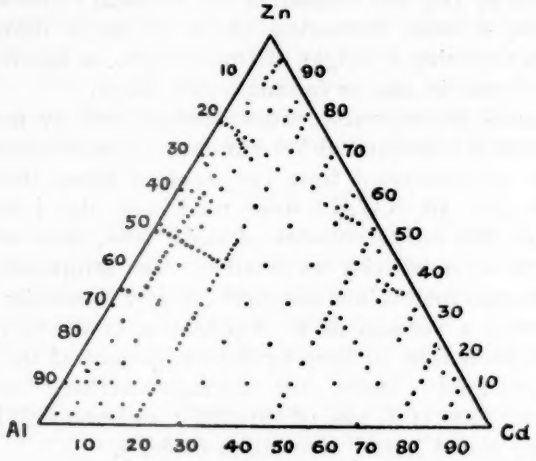


Fig. 1. Regional Diagram. Alloys Investigated.

fact that the alloys were allowed to solidify in a perfectly undisturbed manner, would seem to involve the risk that the observations might be vitiated by errors due to surfusion. With the apparatus used in this work, surfusion phenomena can, however, be readily detected by the occurrence of a rise of temperature following the first arrest of cooling and, although small rises of temperature of this nature were occasionally observed, a prolonged arrest at a definite maximum temperature was invariably obtained, showing that errors from surfusion had been avoided. In the study of the cooling-curves, the cooling of the same ingot has in many cases been repeated three or more times in order to eliminate the possibility of mistaking small irregularities due to experimental error for minor heat evolutions. After three remeltings, if doubt has still existed regarding any alloy, a new mixture has been prepared and

Fig. 3.

[To face p. 1646.]

Fig. 2.

a series of fresh determinations made. A general idea of the distribution of alloys investigated over the complete ternary system is indicated by the regional diagram of Fig. 1.

The positions of the dots denote the compositions of the ternary alloys prepared.

The Ternary System.

The constitutional investigation, originally intended to be confined to the aluminium corner, was ultimately extended to cover the whole concentration plane, and from the data obtained, it has been possible to establish :

1. The *liquidus* surface for the complete system.
2. The approximate area, critical temperature and critical concentration of the biliquidal field which overlies the *liquidus* surface.
3. The constitutional conditions obtaining below the *liquidus* surface for the greater proportion of the ternary system, down to a temperature at which all measurable change has ceased.
4. The influence of each of the metals upon the miscibility of the other two.
5. The microstructure of representative samples.

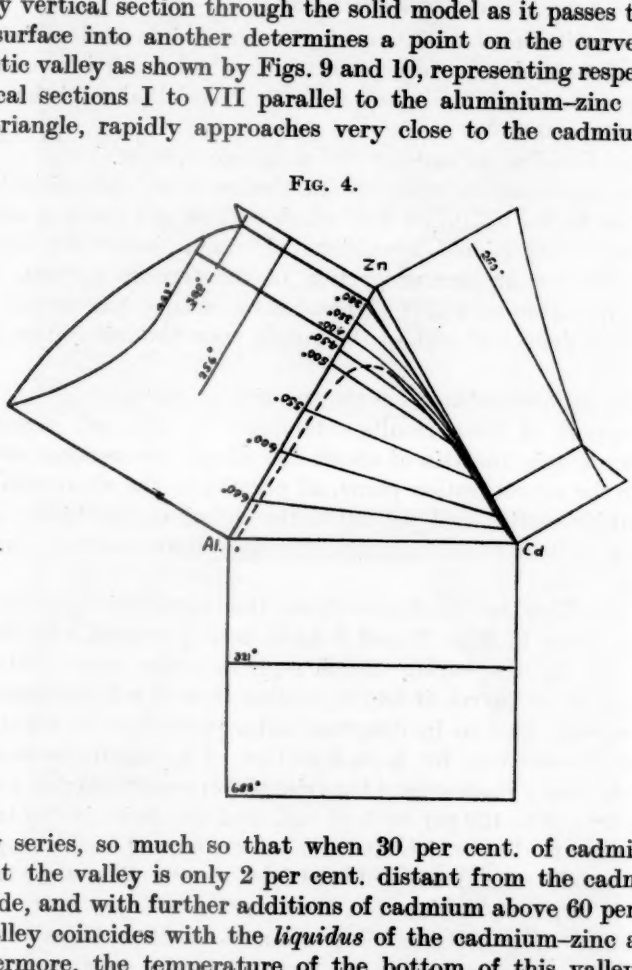
In support of these results established by thermal, chemical,* and microscopic analysis of about 230 alloys, ten vertical sections through the concentration plane, all parallel to the aluminium–zinc side and six sections, all parallel to the cadmium–zinc binary series, together with vertical sections through four tie-lines, are put forward.

(*a*) *The* Liquidus *Surface.*—From the observations made, the models shown in Figs. 2 and 3 have been prepared. In these is shown the *liquidus* surface which represents the locus of the first arrest point on curves of alloys, cooling from the liquid state. In these models, as also in diagrams subsequently to be considered, the usual procedure for representation of a ternary system has been followed. Each side of the triangle represents mixtures of two metals from 0 to 100 per cent. of each and any point in the triangle represents an alloy which contains an amount of each component proportional to the distance of the point from the side of the triangle which is opposite to the apex representing 100 per cent. of that component. Fig. 4 shows the relation of the three binary systems to the *liquidus* isothermals in the ternary system, drawn at intervals of 50°. Figs. 2 to 4 indicate that the most prominent features of the *liquidus* surface are :

* Only a sufficient number of the alloys was chemically analysed to serve as a check upon the compositions resulting from the melting together of the exactly weighed constituents. The loss on melting was experimentally found to be negligible.

(i) A valley or trough joining almost linearly the eutectic at 94·4 per cent. of zinc in the aluminium–zinc with that at 17·4 per cent. of zinc in the cadmium–zinc series. This valley appears as an intersection between the surfaces of trivariant equilibrium between a single crystalline variety and homogeneous solutions. Every vertical section through the solid model as it passes through one surface into another determines a point on the curve. The eutectic valley as shown by Figs. 9 and 10, representing respectively vertical sections I to VII parallel to the aluminium–zinc side of the triangle, rapidly approaches very close to the cadmium–zinc

FIG. 4.



binary series, so much so that when 30 per cent. of cadmium is present the valley is only 2 per cent. distant from the cadmium-zinc side, and with further additions of cadmium above 60 per cent. the valley coincides with the *liquidus* of the cadmium–zinc alloys. Furthermore, the temperature of the bottom of this valley continuously falls from 380° in aluminium–zinc alloys to 268° at the cadmium–zinc eutectic point into which it finally merges.

(ii) A smooth surface sloping down away from the aluminium-cadmium binary series mainly in the direction of the zinc corner, but sloping slightly also toward the zinc–cadmium series. This sloping surface is continuous until the zinc–cadmium binary series

is almost reached, where a steep drop then occurs, terminating for alloys with more than 18·0 per cent. of zinc in the eutectic valley already referred to in (i) above.

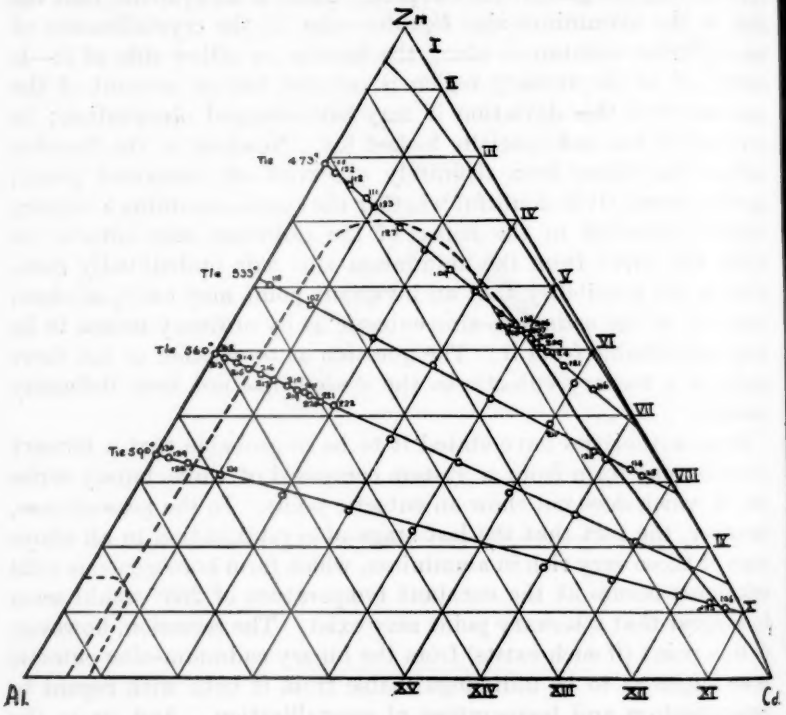
The steepest portion of the *liquidus* is near the cadmium–zinc binary series, where, in certain alloys containing 80 or more per cent. of cadmium, there is actually an increase in the temperature of the *liquidus* of nearly 300° by the addition of only 5 per cent. of aluminium. Over that part of the *liquidus* surface defined by alloys containing 0 to 10 per cent. of aluminium and 30 to 100 per cent. of cadmium, the gradient is steepest. There is no evidence that the kink in the aluminium–zinc *liquidus*—due to the crystallisation of two different substances along the branch on either side of it—is continued as the ternary region is entered, but on account of the minuteness of this deviation it may have escaped observation; in any case it was not specially looked for. Nowhere in the *liquidus* surface has there been definitely observed an invariant point; in other words, it is doubtful whether the system contains a ternary eutectic, although in the region of the cadmium–zinc eutectic to which the curve from the aluminium–zinc side undoubtedly runs, there is the possibility that an invariant point may exist, so close, however, to the cadmium–zinc eutectic as by ordinary means to be indistinguishable from it. The question as to whether or not there really is a ternary eutectic in the system has not been definitely decided.

Some authorities have stated it to be improbable that a ternary eutectic may form from a system composed of three binary series one of which does not show an eutectic point. In the present case, however, the fact that the last stage of crystallisation in all alloys (except those very rich in aluminium, which form homogeneous solid solutions) occurs at the constant temperature of 268° would seem to suggest that a ternary point may exist. The recession, however, of this point (if such exists) from the binary cadmium–zinc eutectic is so slight as to be indistinguishable from it both with regard to concentration and temperature of crystallisation. And, as in the present research no special investigation of these minute concentration differences has been made, the position of this point is assumed to be practically coincident with the binary eutectic in cadmium–zinc alloys.

(*b*) *The Biliquidal Field.*—As has been already noted in consideration of the binary systems, one, the aluminium–cadmium series, represents a rather unique type in which there is apparent complete immiscibility in both liquid and solid states, so that the molten alloys consist of two liquid layers. As would be expected, these conditions persist as the ternary field is entered and an important

feature, therefore, of the *liquidus* surface is that it is overlain by an immiscible zone, giving to it a characteristic flat shape, sloping towards the centre of the triangle and standing in contrast to the general inclination of the *liquidus* surface. In proceeding to effect a thermal determination of the boundaries of this surface, it was decided to investigate four vertical plane sections passing through the entire figure in the directions of four tie-lines about evenly distributed between the supposed position of the critical point and

FIG. 5.



the cadmium–aluminium side. It was first necessary to locate the tie-lines in the concentration plane and this was done as follows:

Along each of the accurately plotted vertical sections I to X parallel to the aluminium–zinc side, measurements were made until a point in the *liquidus* was reached at some predetermined temperature. The horizontal distance of this point from the aluminium-cadmium side was then measured and set off on the concentration plane shown in Fig. 5.

This, then, represents one point on one tie-line. The temperatures of the tie-lines investigated are 590°, 560°, 533° and 473°

(Fig. 6), thus for the first tie-line, working in series parallel to the aluminium–zinc side, the sectional diagrams (representing cadmium 5, 10, etc., per cent.) are traversed until verticals from the con centration plane cut the *liquidus* in the point corresponding to 590°, the distances traversed are measured and set off in the concentration plane, giving the points on the tie-line at 590°. By proceeding in this way with all the sectional diagrams and for all the ties, a number of points are located which, for each tie, lie approximately in one straight and isothermal line.

It will be seen on referring to Fig. 5 that these concentrations lie remarkably close to the lines drawn through them, showing that the determinations are accurate to a high degree. The inclination

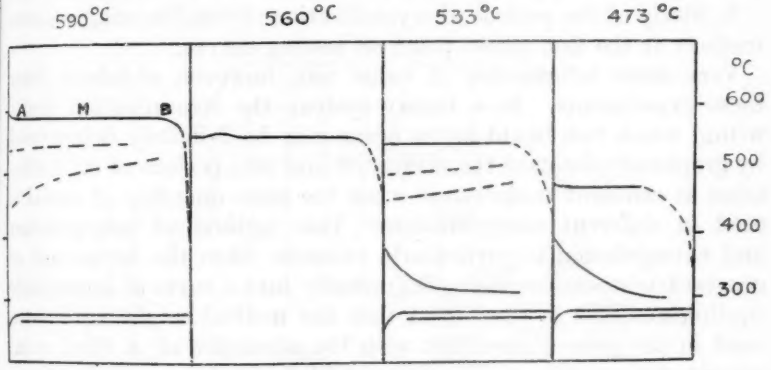


Fig. 6. Tie Lines.

to one another which the ties exhibit is caused by the disproportional alteration of the composition of each as cadmium is added to the mixture of two liquid phases. During the first period of solidification of the double phase liquid, there are three phases present—namely the two liquids and the primary solid, so that the temperature does not remain stationary, and therefore the intersection of the boundary of the biliquidal field with the *liquidus* surface is not an isothermal line. But an isothermal drawn upon the *liquidus* and double-liquid field might show two abrupt changes of direction at the two points of intersection of these surfaces at that temperature. Thus the concentrations at which the temperature changes rapidly determine the end-points of each tie-line. But, in the present instance, these conditions do not quite obtain and extensions of the monotectic horizontals drawn to intersect the aluminium–zinc binary *liquidus* curves show practically the same temperature along their length on this side, exhibiting no change of direction at the boundary of the biliquidal field. Further, as the

ternary field is entered by way of the vertical sections through the tie-lines, approaching the zinc corner it becomes increasingly difficult to determine the points at which the ties meet the sloping *liquidus* curves. These conditions considerably militate against accurate determinations of the boundary and render its exact fixation by this method, on the aluminium–zinc side at least, a matter of some difficulty. Various means were employed in an endeavour to determine the location of this boundary on the aluminium–zinc side, among which may be mentioned :

1. Microstudy of normally cooled neighbouring concentrations along a tie-line.

2. Macrostudy of alloys retained molten in glass tubes for prolonged periods in order to allow of separation of the layers.

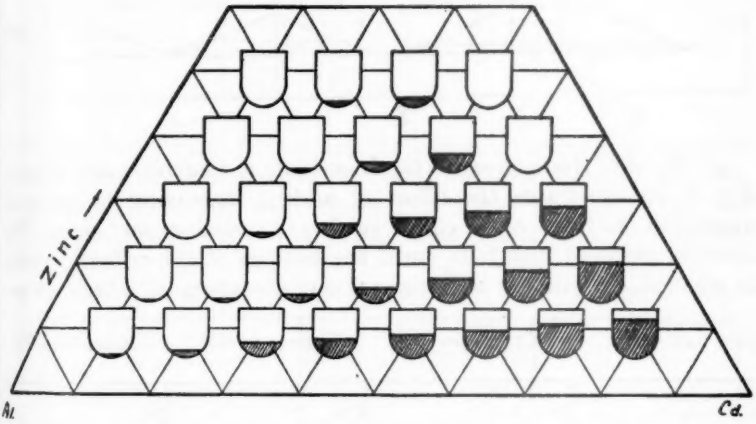
3. Study of the periods of crystallisation of neighbouring concentrations at the first arrest point on cooling curves.

Very little information of value was, however, obtained from these experiments. In a binary system, the concentration limits within which two liquid layers occur may be definitely determined by graphically locating the maximum and zero periods of crystallisation at constant temperature when the same quantity of metal is used in different concentrations. This method of interpolation and extrapolation is particularly valuable when the horizontal of constant temperature changes gradually into a curve of incomplete equilibrium and it was hoped that the method might have been used in the present case, but with the admission of a third component the system acquires one additional degree of freedom, whereby the two liquid phases may remain in equilibrium with the primary crystalline phase throughout a range of temperature. During crystallisation of the latter from any biliquidal mixture, the temperature falls and the two conjugate liquids change in composition, finally merging into one. The cooling curves, however, fail to indicate points at which one solution separates into two, or two solutions merge into one during the process of crystallisation, so that it is impossible to verify the direct determination of the end-points of any tie-line by critical study of the cooling curves alone. The extent, therefore, of the biliquidal field, which is well defined on the one side near the cadmium–zinc binary series, is less accurately determined on the aluminium–zinc side, as shown dotted in Fig. 5. It is noticeable that the biliquidal portions of the primary branches shown in the vertical sections parallel to the cadmium–zinc side are slightly concave, viewed from above, but the limiting biliquidal concentrations are not sharply defined by this feature. Further, the surfaces located beneath the primary surface of the solid solution rich in aluminium bear no distinguishing marks due

to the presence of a biliquidal area over the latter. In Fig. 7, which is self explanatory, an approximation to the shape and extent of the biliquidal field is shown. The diagram was constructed by data derived from a macro-examination of neighbouring alloy concentrations in sectioned ingot form, the relative amounts of upper and lower alloy layers being estimated. The diagram is not accurate, however, and is not a true representation of the location of the biliquidal boundary. From Fig. 5 it may be estimated, although somewhat approximately, that the critical concentration is in the neighbourhood of aluminium 11, cadmium 25, and zinc 64 per cent., whilst the critical temperature would be at about 468°.

(*c*) *Effect of Zinc on the Miscibility of Aluminium and Cadmium.*—The primary object of the three following curves is to show the

FIG. 7.



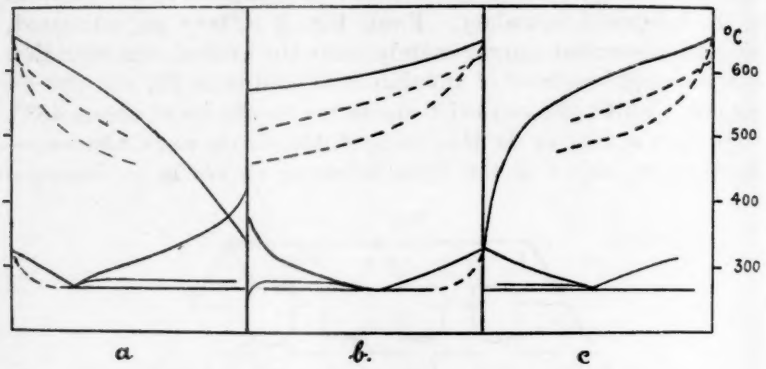
variation of temperature induced in the *liquidus* by the addition of the third metal to equal proportions of the other two.

Fig. 8 (*a*) illustrates the effect of adding increasing amounts of zinc to a mixture of equal proportions by weight of aluminium and cadmium. It is a section of the solid model along a median through zinc and the middle point of the aluminium–cadmium base. The point of primary crystallisation falls continuously until alloy Cd 5, Zn 90, where the binary eutectic valley is encountered; further on, a rise in the freezing points of the alloys is recorded to that of pure zinc. The binary eutectic arrest falls at first until alloys Cd 40, Zn 20, and Cd 30, Zn 40 are reached, between which it lies on the lower ternary eutectic plane, afterwards rising to the aluminium–cadmium series.

(*d*) *Effect of Cadmium on the Miscibility of Aluminium and Zinc.*—Fig. 8 (*b*) shows the effect of increasing quantities of cadmium upon

the freezing point and *solidus* lines of mixtures of equal weights of aluminium and zinc. The rise in the temperature of primary crystallisation is at first very slight, until the content of cadmium reaches 60 per cent., after which the rise is more rapid, continuing with further additions to the freezing point of aluminium.

FIG. 8.



(*e*) *Effect of Aluminium on the Miscibility of Cadmium and Zinc.*—Fig. 8 (*c*) illustrates the effect of adding increasing amounts of aluminium to mixtures of equal weights of cadmium and zinc. The freezing point at first falls, until the bottom of the eutectic valley is reached, and thence rises remarkably steeply until about 10 per

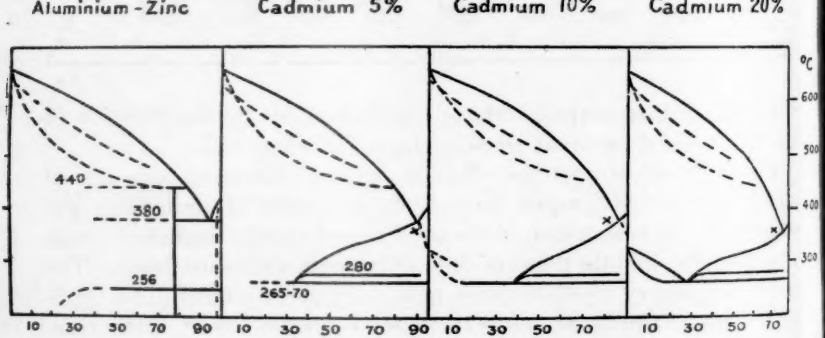


Fig.9.

cent. of aluminium is present, after which the slope is more gradual, becoming almost linear from this point to the melting point of pure aluminium. This figure is a section of the solid model along a median through the aluminium corner and the middle point of the cadmium–zinc base.

The lower lines of these three diagrams may not properly be discussed here.

(*f*) *The Constitution below the* Liquidus.—The cooling curves of alloys over the area of the whole concentration plane furnish

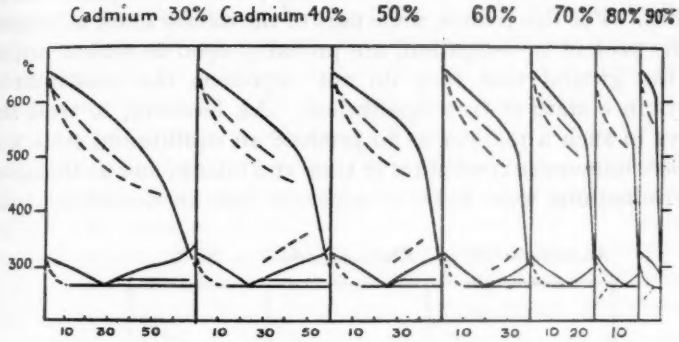


Fig. 10.

sufficient data for the determination, with fair precision, of the solid constitution, certain exceptions, which will be referred to later, being made. The vertical sections I to XV of Figs. 9, 10, 11, and 12 and the perspective view of the wire model (Fig. 3) illustrate

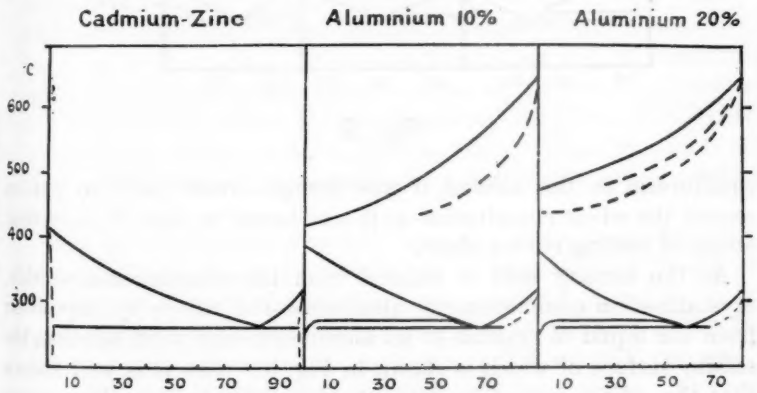


Fig. 11.

the principal conclusions which have been arrived at. By commencing at the aluminium–zinc side and considering successive sections (Figs. 9 and 10) through the solid triangle, it will be seen that the features of this binary series only to a slight extent persist as the ternary field is entered. The earlier diagram of Rosenhain

and Archbutt for the aluminium–zinc series, worked out, up to a content of 60 per cent. of zinc, mainly on the data derived from a study of cooling curves, is in better accord with the thermal results of the present investigation than the diagram lately put forward by Hanson and Gayler as representing practically equilibrium conditions. For this reason, some part of the *solidus* lines, as suggested in the present investigation, are probably open to serious criticism on the ground that they do not represent the constitution of alloys in a state of true equilibrium. As, however, to treat many alloys in such a manner as to produce an equilibrium state would involve immense expenditure of time and labour, and as the *liquidus* determinations were believed accurate and unaffected by lack of

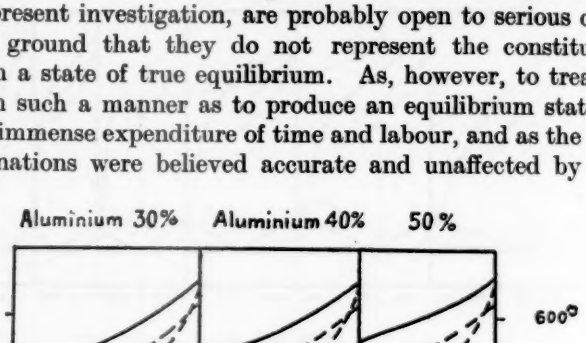


Fig. 12.

equilibrium in the *solidus*, it was thought worth while to put on record the whole constitution as it was found to exist by a critical study of cooling curves alone.

As the ternary field is entered from the aluminium–zinc side, crystallisation commences for aluminium-rich alloys by deposition from the liquid of crystals of an aluminium–zinc solid solution, the *solidus* surface of which is shown in Fig. 3. Now it is well known that the *solidus* cannot be determined directly from cooling curves alone, except in some exceptional case, such, for example, as where the last stage of solidification occurs at an invariant point. It is improbable, therefore, that the *solidus* determined in the present case by the method of curvature of the cooling curves is very accurate. But, by working under identical conditions as regards mass of metal and rate of cooling and taking complete solidification to correspond to a position on the inverse-rate curves a little above the point at

which the rate of cooling returned to that of the melt before solidification commenced, it was believed that at least comparable results would be obtained. Furthermore, each succeeding series containing constant percentages of cadmium could be compared with the aluminium–zinc binary series. On account, however, of the uncertainty which existed as to the exact location of the *solidus* surface lying close beneath the primary *liquidus*, it is shown as a dotted line, indicating that its position is not claimed to have been exactly determined. With as little as 5 per cent. of cadmium, a marked change occurs in certain lines of the aluminium–zinc diagram. The peritectic line, which normally lies at 443° in aluminium–zinc alloys, appears still to persist, but at a slightly elevated temperature (445°). The eutectic horizontal which, according to the earlier binary diagrams above referred to, continues only to a concentration of 40 per cent. of aluminium at 380°, now slopes smoothly from the base of the valley to about 50 per cent. of aluminium, and thereafter much more steeply, ultimately intersecting the ternary eutectic plane at 268° and 62 per cent. of aluminium. This sloping line, though at a somewhat higher temperature, is also exhibited in a vertical section containing only 2 per cent. of cadmium and, like its counterpart on the zinc side of the eutectic valley, really represents a section through the binary eutectic surface. Further, in the series containing 5 per cent. of cadmium, two lower lines practically horizontal and lying at 268°, respectively, replace the one, which in aluminium–zinc alloys occurs at 256°, the lower limit of stability of the compound Al_2Zn_3. It was apparent that one of these lines, probably the upper, must originate in the aluminium–zinc series and represent the lower limit above referred to; the other, as it occurred in all alloys of the ternary system, except those in which solid solutions are formed, presumably represented the ternary eutectic arrest.

In order to ascertain which of these was which, a carefully determined vertical section parallel to the cadmium–zinc side and containing 20 per cent. of aluminium was prepared (Fig. 11); in this, concentrations were made to advance into the ternary region from the aluminium–zinc side, by successive additions of 2 per cent. of cadmium until 12 per cent. of the latter had been added. The result clearly showed that the addition of only 2 per cent. of cadmium raises the temperature of the line representing final decomposition of the compound Al_2Zn_3 from 256° to 276°, a very surprising increment, successive additions of cadmium making no further alteration of its temperature; but when 5 to 6 per cent. of cadmium is present, a new lower arrest at 268° makes its appearance and, presumably, represents the ternary eutectic plane. These planes

are shown in sectional form in Figs. 9 to 12 and as a whole in perspective by Fig. 3. In further support of the supposition above made as to their origin, it may be observed that the duration of arrests (measured by the usual approximate methods) clearly show an increase for the upper of the two planes as the aluminium–zinc side is approached by commencing from near the cadmium–zinc eutectic where this upper plane terminates; the heat evolutions there being very weak. For the lower of the two planes, however, the arrests commencing to appear in alloys containing 5 per cent. of cadmium are markedly smaller than those observed in the vicinity of the cadmium–zinc binary eutectic, and furthermore these arrests are found on all curves except those in the extreme aluminium corner of the diagram, where evidence is available to show that solid solutions form, all measurable change in which has ceased at a high temperature of about 550°.

As successive sections parallel to the aluminium–zinc side are considered (Figs. 9 and 10), features similar to those already described are encountered, the binary eutectic lines continually shortening and sloping less steeply until, in a section containing 82 per cent. of cadmium, they have disappeared. In all these sections, the lower plane which, on the cadmium–zinc side runs to intersect the binary series at the temperature of the eutectic horizontal, stops short on the aluminium–zinc side, as previously indicated, at about 5 per cent. distant from the binary system while on the aluminium–cadmium side it appears to slope up to meet the line at constant temperature and corresponding to the freezing point of pure cadmium in this series. This curvature, however, which was determined as carefully as possible by the point at which the rate of cooling, as shown by the curves, returned to that obtaining before arrestation commenced, would seem to suggest that the lower plane does not represent the locus of ternary eutectic halts.

Passing on now to consider vertical sections parallel to the cadmium–zinc side and obtained by locating the temperatures of primary and secondary crystallisation on sections I to X (Figs. 9 and 10) at the concentrations of intersection with those of Figs. 11 and 12, the conditions above described are again brought out, only the features of the cadmium–zinc binary series are this time reproduced. Thus in vertical section XI the two branches of the original cadmium–zinc *liquidus* are seen to be little altered, except that the one originally representing primary crystallisation of zinc occurs now at a somewhat lower temperature. The sloping plane, falling from the aluminium–cadmium side to meet the twisted binary eutectic surface in a gutter of constant and lowest temperature, is clearly shown in this and similar sectional diagrams. Sections

containing more than 50 per cent. of aluminium cease to exhibit new features and are therefore not reproduced. In connexion with several of the vertical sectional diagrams (Nos. III, IX, and XII), some typical cooling curves are shown in Fig. 13, but their characteristics call for no special comment.

It may thus be inferred by collective consideration of all these sectional diagrams that the principal features of the *solidus* constitution include :

1. A *solidus* surface lying beneath the *liquidus ;* only approximately determined in the present investigation on account of the difficulty of exactly locating it by a critical study of cooling curves alone.

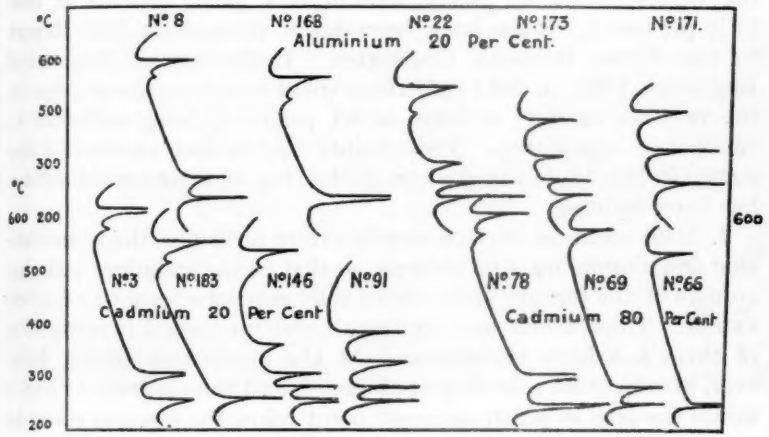


Fig. 13 Typical Cooling Curves.

2. A binary eutectic surface, consisting of two twisted planes sloping away from the bottom of the eutectic valley and intersecting the lowest plane in an almost straight line.

3. A sloping surface from the aluminium–cadmium side, originating at the temperature of the lower horizontal in this series (321°), meeting one of the binary eutectic surfaces, and forming a gutter which runs from the cadmium–zinc eutectic to the aluminium–zinc side at the termination of the binary eutectic horizontal.

4. A plane extending entirely beneath the binary eutectic surfaces, at the boundaries of which it terminates and originating in the aluminium–zinc binary series at 256°, and being at once raised to 276° by the addition of as little as 2 per cent. of cadmium and remaining at this temperature throughout the concentration range of its existence.

5. A plane at 268°, the temperature of the binary cadmium–

zinc eutectic, extending over the whole ternary concentration plane except in the extreme aluminium corner, where the solid solutions which are formed at a high temperature undergo no further change. The greatest intensity of heat evolution for the arrests locating this plane are at or near the binary cadmium–zinc eutectic, seeming to indicate that the plane is caused by the solidification of a ternary eutectic substance.

In addition to the above, certain other minor features are noticeable :

1. In most of the sections parallel to the aluminium–zinc side a line of arrest points located just below the *liquidus* curve is shown. These points originate in the aluminium used, which, although of the highest available purity, contained a small amount of iron (0·19 per cent.). It has lately been shown (Rosenhain, 11th Report to the Alloys Research Committee. Institution of Mechanical Engineers, 1921, p. 201) that these small arrest points are due to the presence of iron, as little as 0·1 per cent. being sufficient to cause their appearance. These points may be seen on some of the curves in Fig. 13, but in the wire model (Fig. 3) their curved surface has been omitted.

2. Solid solutions are to a certain extent formed in the cadmium–zinc and aluminium–zinc systems, so that at the cadmium and zinc corners of the tertiary space model solid solutions form to a limited extent. These limits are very small and no special investigation of them has been undertaken. At the aluminium corner, however, greater solid solubility is observed, and the diagram of Fig. 5 shows the area in which no arrest point below the *liquidus* could be observed on cooling curves, thus indicating that all alloys lying within this region are homogeneous solid solutions, a fact which is confirmed by microscopic examination subsequently to be considered.

Microstructures.

Photomicrographs illustrative of the structures observed over the whole ternary field have been prepared, but it is obviously not possible at this stage fully to discuss the complex constituents which are encountered. Some of the simpler aspects of the subject may, however, be considered.

For the purpose of microscopic examination, specimens were, as a rule, cut from the ingots used for cooling-curve determinations, and in all cases complete vertical sections were employed so as to enable observation of the segregation phenomena to be made. Polishing of the specimens, especially near the aluminium corner, proved a matter of some difficulty, but by use of damped alumina on a chamois leather pad sufficiently satisfactory results were

FIG. 14. FIG. 15.

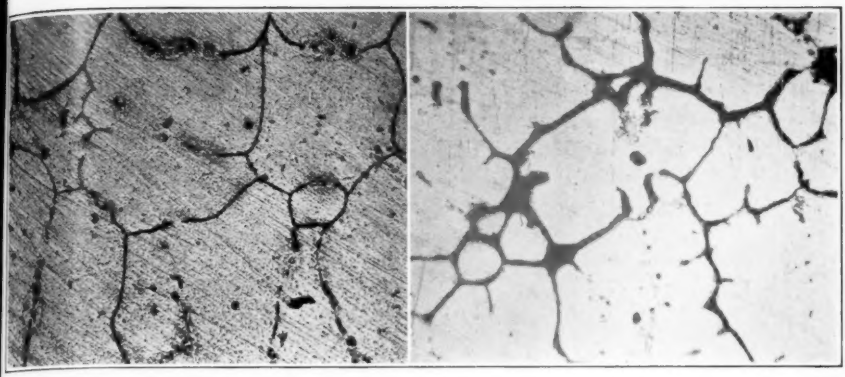


FIG. 16. FIG. 17.

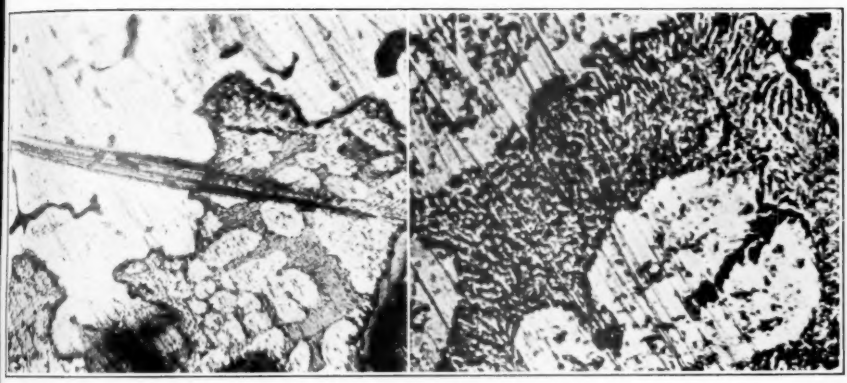


FIG. 18. FIG. 19.

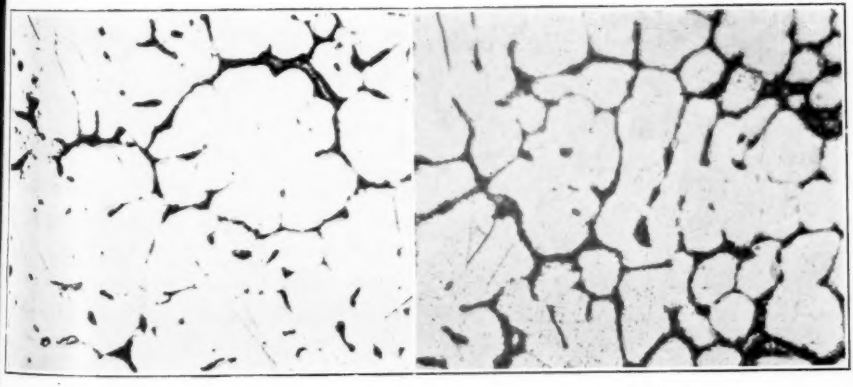


FIG. 14.—Cd 2, Zn 10. Slowly cooled from above *liquidus* to 200° × 25.
FIG. 15.—Cd 20, Zn 20. ,, ,, ,, ,, ,, to 200° × 25.
FIG. 16.—Cd 20, Zn 20. ,, ,, ,, ,, ,, to 200° × 25.
FIG. 17.—Cd 20, Zn 20. ,, ,, ,, ,, ,, to 200° × 250.
FIG. 18.—Cd 80, Zn 10. ,, ,, ,, ,, ,, to 200° × 25.
FIG. 19.—Cd 20, Zn 30. ,, ,, ,, ,, ,, to 200° × 25.

[*To face p.* 1658.]

FIG. 20.

FIG. 21.

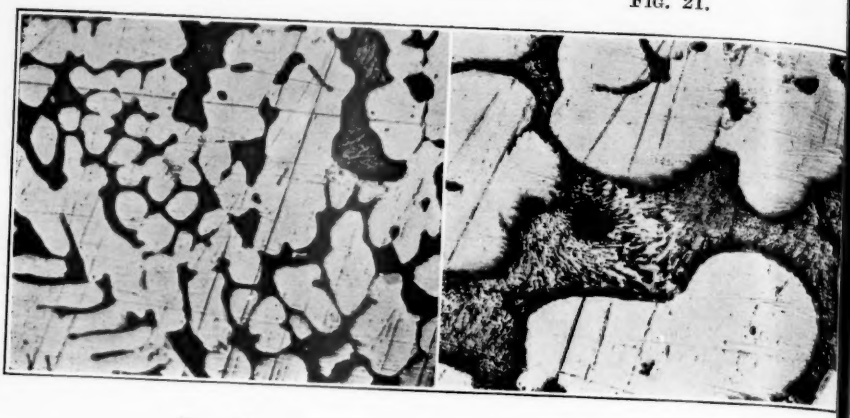


FIG. 22.

FIG. 23.

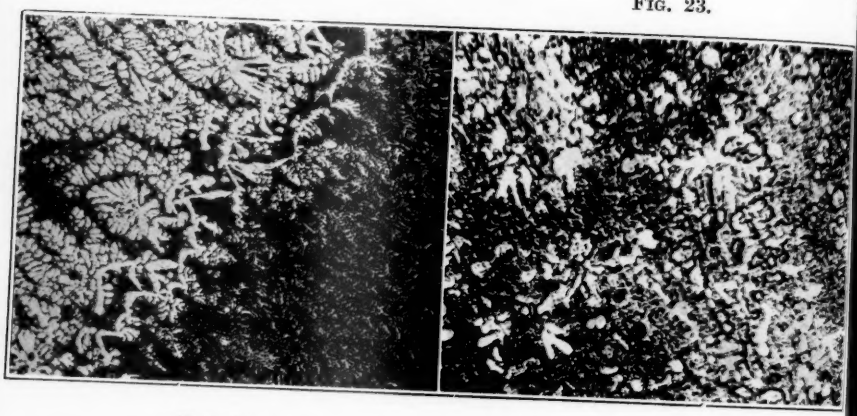


FIG. 24.

FIG. 25.

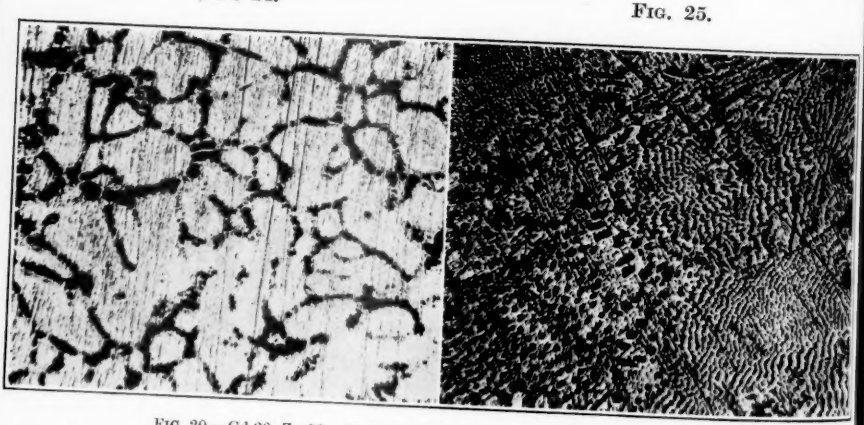


FIG. 20.—Cd 20, Zn 30. Slowly cooled from above *liquidus* to 200° × 25.
FIG. 21.—Cd 20, Zn 30. " " " " " to 200° × 150.
FIG. 22.—Cd 40, Zn 40. " " " " " to 200° × 15.
FIG. 23.—Cd 40, Zn 40. " " " " " to 200° × 25.
FIG. 24.—Cd 60, Zn 30. " " " " " to 200° × 25.
FIG. 25.—Cd 60, Zn 30. " " " " " to 200° × 50.

obtained. For etching most of the aluminium-rich alloys, immersion for 1 minute in a 10 per cent. solution of caustic soda, followed by a dip in chromic acid—to remove the black deposit—gave good results; but other reagents, including weak nitric acid and 10 per cent. ferric chloride solution, were also employed. In considering the structures which are observed, it is convenient to divide the alloys of the system into three groups; the first of these, lying near the aluminium corner, includes compositions which on microscopic examination show a single homogeneous constituent. The concentration limit of existence of such alloys is small relative to the whole ternary field and is defined by the dotted enclosure shown in Fig. 5, the compositions being approximately aluminium plus zinc 0 to 11% and cadmium 0 to 4%.

The single constituent of which the alloys are composed represents the γ-solid solution * of the aluminium–zinc series in which cadmium is dissolved to an amount not exceeding about 4 per cent. A typical photomicrograph of an alloy containing aluminium 88, zinc 10, and cadmium 2%, is shown in Fig. 14.

The second group of alloys occupies a rather larger section of the concentration plane, and comprises those which lie within the area of liquid immiscibility and may, on cooling, separate into two layers.

Alloy Cd 20, Zn 20 (Figs. 15, 16, and 17) is illustrative and shows (Fig. 15) a portion of the upper layer consisting of the dark-etching constituent at the boundaries of aluminium-rich solid solution grains. Fig. 16, representative of the bottom layer, shows the dark-etching grain boundaries of the light-etching solid solution to persist, while scattered throughout the layer are large irregular masses of the former in a coalesced state, and containing within themselves still another ill-defined substance. Fig. 17 is a photomicrograph of one of these complex areas and clearly shows the presence of an eutectic substance.

The gradual change in the proportion of upper and lower layer as the concentration plane is traversed from the aluminium–zinc to the cadmium–zinc side is well shown by photomicrographs of such alloys as Cd 2, Zn 10, (Fig. 14) to Cd 80, Zn 10 (Fig 18). Thus commencing at the aluminium–zinc side and proceeding in the direction indicated, there is a uniform increase of the heavier constituent, first merely producing thicker grain boundaries and later resulting in the formation of a definite lower layer. Alloy Cd 5, Zn 10 shows a small amount of boundary material, whereas that of Fig. 14 (outside the immiscible zone) shows none, and when Cd 80,

* The γ-constituent of aluminium–zinc alloys occurs in the normally cooled compositions containing between 0 and 18 per cent. of zinc.

Zn 10 is reached there is in the upper layer a considerable distribution of the network constituent, besides also a thick lower layer representing approximately three-quarters of the whole ingot and of the complex nature described for alloy Cd 20, Zn 20 (Fig. 16).

Alloys Cd 20, Zn 30 and Cd 40, Zn 40 lying still within this region, show similar features; thus Figs. 19 and 20 of alloy Cd 20, Zn 30 are representative of the upper and lower layers, Fig. 21, at higher magnification, showing the complexity and eutectic nature of the boundary material. Of alloy Cd 40, Zn 40, Fig. 22 shows the boundary between the two layers, the upper of which consists of large, white, dendritic leaves surrounded by a complex material from the lower layer (Fig. 23). Two photomicrographs of alloy Cd 60, Zn 30 are reproduced; Fig. 24 represents the upper portion, constituting the main bulk of the ingot; Fig. 25 shows the lower layer, consisting of perfect eutectic grains exhibiting the typical rod or dot structure and beautiful laminations. It is interesting to note in this connexion that at the first etch by treatment with 10 per cent. ferric chloride solution for ½ a minute this eutectic structure was clearly developed, but on re-polishing and re-etching in order to improve the definition, the structure disappeared and could by no means be reproduced. Microstructures of alloys lying near the zinc corner of the concentration plane exhibit considerable complexity and are not described.

In conclusion, the author wishes to acknowledge especial indebtedness to Professor T. Turner, M.Sc., A.R.S.M., F.I.C., for granting every facility for carrying out the investigation in his laboratories and for his continued interest and advice.

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CCXVII.—*A Phase Rule Study of the Cupro-, Argento-, Auro- and Thallo-cyanides of Potassium.*

By HENRY BASSETT and ALEXANDER STEVEN CORBET.

FOR several reasons an investigation of these compounds appeared to be of interest. The cupro-, argento- and auro-cyanides are familiar substances and their uses in analysis, in metallurgy, and in electroplating are well known. Of the remaining metals, thallium alone may possibly form complex cyanides in which the metal is

univalent and present in the anion. A comparison between any potassium thallocyanides and the corresponding cupro-, argento- and auro-cyanides would therefore be of interest, if only in completing the series. Mercury forms neither a mercurous cyanide nor complex mercurocyanides and attempts to prepare these substances by adding excess of potassium cyanide to solutions of mercurous salts resulted in formation of mercuric cyanide and deposition of mercury.

Also it is instructive to consider the compounds in the light of the electronic theory of valency.

From a preparative point of view, while the cuprocyanides of potassium have been investigated by several workers, the argento- and auro-cyanides have received less study, and little attention has been directed to complex thallium cyanides.

Electrolytic investigations of the subject have indicated the presence of compounds in solution which, up to now, have not been isolated. The subject has been considered from a thermal point of view also, Truthe having investigated the binary systems KCN–CuCN and KCN–AgCN.

Ordinary methods of approaching the problem are attended with some degree of uncertainty in that it is often a matter of no little difficulty to obtain any given compound in a reasonably pure state, and, in consequence, there may be some doubt as to whether or not a definite compound is present.

When this subject is considered in the light of the phase rule, and a system such as potassium cyanide–metal cyanide–water is investigated, this difficulty can be surmounted. The results obtained from the analyses of the liquid and moist solid phases in an equilibrium mixture can be plotted by one of the standard graphical methods, and it is thus possible to arrive at the composition of the pure solid without the necessity of isolating it.

(*a*) *The System Potassium Cyanide–Cuprous Cyanide–Water.*

Previous investigators have described three well-defined cuprocyanides of potassium, namely, $K_3Cu(CN)_4$, which was discovered by Gmelin and more minutely examined by Rammelsberg (*Pogg. Ann.*, 1837, **42**, 111); $KCu(CN)_2$, discovered by Ittner and investigated by Gmelin ("Handbook of Chemistry," 1853, VIII, 4), Rammelsberg (*loc. cit.*), Itzig (*Ber.*, 1902, **35**, 106), and Treadwell and Girsewald (*Z. anorg. Chem.*, 1904, **38**, 92); and $KCu_2(CN)_3,H_2O$, which was accidentally discovered by Schiff and Bechi (*Annalen*, 1866, **138**, 24) and examined by Itzig (*loc. cit.*) and Treadwell and Girsewald (*loc. cit.*; compare, however, Grossmann and Forst, *Z. anorg. Chem.*, 1905, **43**, 94).

The existence of other potassium cuprocyanides is uncertain. Truthe, who investigated the binary systems KCN–CuCN and KCN–AgCN (Inaug. Dissert. Göttingen, 1912) and adduced evidence for the existence of the compounds $K_3Cu(CN)_4$, $KCu(CN)_2$, and $KCu_2(CN)_3$, considered that under the conditions prevailing during those experiments, the compounds $KCu_3(CN)_4$ and $K_3Cu_2(CN)_5$ might exist. From the results obtained by titrating solutions of potassium cyanide and copper sulphate in absence and presence of ammonia, Treadwell and Girsewald (*loc. cit.*) considered it probable that compounds such as $K_2Cu(CN)_3$ and $K_3NH_4[Cu(CN)_3]_2$ might exist in solution. This view received support from the investigations of Kunschert (*Z. anorg. Chem.*, 1904, **41**, 359), who demonstrated the presence of $[Cu(CN)_4]'''$ and $[Cu(CN)_3]''$ ions in aqueous solutions of copper in potassium cyanide by Bodländer's electrolytic method. The potassium cuprocyanide, $K_2Cu_3(CN)_5$, described by Rammelsberg (*Pogg. Ann.*, 1848, **73**, 117) was regarded by Itzig (*loc. cit.*) as a mixture of $KCu_2(CN)_3$ and potassium cyanide.

We have been unable to prepare the salt $KCu_2(CN)_3,H_2O$ by Itzig's method, by which, however, $K_3Cu(CN)_4$ was often obtained, or by the method of Treadwell and Girsewald, which gave a mixture containing a much higher percentage of cuprous cyanide, but obtained it in small quantity, and also the tripotassium salt, in the way described on p. 1670.

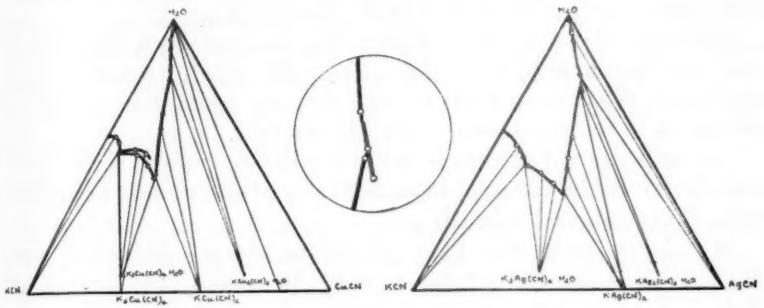
In view of the difficulties attending the preparation of the potassium cuprocyanides, the investigation of the system KCN–CuCN–H_2O is of no little interest. The system is a three-component one and was examined at 25°. As was expected, it was found that the compounds $K_3Cu(CN)_4$, $K_3Cu(CN)_4,H_2O$, $KCu(CN)_2$, and $KCu_2(CN)_3,H_2O$ are all capable of existing at this temperature, but there was no indication of a compound $K_2Cu(CN)_3$.

The results of the analyses of the liquid and moist solid phases in equilibrium are given in Table II on p. 1671 and represented graphically in Fig. I. The figures in the potassium cyanide columns for the liquid phase refer to actual cyanide and not to cyanide plus hydroxide. It is true that, in solutions containing only potassium cyanide and small amounts of potassium hydroxide in equilibrium with solid potassium cyanide, the total potassium content is approximately constant. It might have been thought, therefore, that, when dealing with the three-component systems considered in this paper, the total potassium content should be plotted rather than the potassium cyanide alone. If this is done, however, the curve for solutions in equilibrium with potassium cyanide is concave to the apex of the triangular diagram corresponding to pure water instead of being convex, as it should be. The use of the

potassium cyanide content alone therefore seems to be justified. The foregoing remarks apply also to the silver, gold, and thallium systems.

Referring to the diagram, it will be seen that the solubility of potassium cyanide in water at 25° is slightly decreased at first by addition of cuprous cyanide, but almost reaches its original value when 5·5 per cent. of cuprous cyanide is present.

FIG. 1. FIG. 2A. FIG. 2.



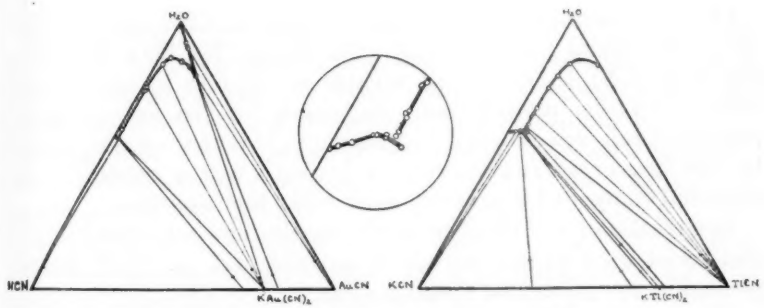


FIG. 3. FIG. 4A. FIG. 4.

The curves for the tripotassium salts are cut by a line joining the point representing 100 per cent. of water to the points giving the compositions of the pure compounds, and these salts alone of the cuprocyanides can be in equilibrium with solutions in which the ratio KCN : CuCN is the same as in the solid phase. The points of intersection of the curves with this line give the solubilities of $K_3Cu(CN)_4$ and $K_3Cu(CN)_4,H_2O$ in water at 25° and in the case of these compounds alone is recrystallisation from water possible. The hydrated tripotassium salt is metastable in contact with solution at 25°.

(b) *The System Potassium Cyanide–Silver Cyanide–Water.*

The compound $KAg(CN)_2$ appears to be the only potassium argentocyanide known hitherto in the solid state (Ittner, Gmelin's "Handbook of Chemistry," 1853, VIII, 29; Rammelsberg, *Pogg. Ann.*, 1836, **38**, 372; Glassford and Napier, *Phil. Mag.*, 1844, [iii], **25**, 66). The crystalline substance to which the last-mentioned workers attributed the formula $KAg(CN)_2,H_2O$ was shown by Baup (*Ann. Chim. Phys.*, 1858, [iii], **53**, 464) to have the composition corresponding with $3KAg(CN)_2,NaAg(CN)_2$.

Although the compound $K_2Ag(CN)_3$ has not been obtained in the solid state, Bodländer (*Ber.*, 1903, **36**, 2878), from electrolytic evidence, considered that it was formed when silver sulphide dissolved in 0·5*N*-potassium cyanide solution.

Truthe's thermal investigations of the binary systems KCN–AgCN and NaCN–AgCN (*loc. cit.*) indicate the existence of only one double salt, $KAg(CN)_2$ or $NaAg(CN)_2$.

We have prepared two crystalline salts, $KAg(CN)_2$ and $K_3Ag(CN)_4,H_2O$, but were unable to make the compound $KAg_2(CN)_3,H_2O$ by a method analogous to that by which the corresponding cuprocyanide was obtained, as the salt $KAg(CN)_2$ invariably resulted.

On investigating the three-component system KCN–AgCN–H_2O at 25° it was found that the compounds $K_3Ag(CN)_4,H_2O$, $KAg(CN)_2$, and $KAg_2(CN)_3,H_2O$ were all capable of existing in contact with solution at this temperature. No curve for the anhydrous tripotassium salt was obtained and attempts to prepare this compound by effecting crystallisation from a boiling solution resulted in the hydrated compound separating as at lower temperatures.

The results of the analyses of the equilibrium mixtures of liquid and moist solid phases are given in Table III (p. 1672) and are plotted in the triangular diagram (Fig. 2).

The compound $KAg(CN)_2$ is stable in contact with solutions of widely different compositions, but the salt $KAg_2(CN)_3,H_2O$ has a very small range of existence, although it can be followed some way into the metastable regions (see Fig. 2A). Silver cyanide has a much greater range of solubility than cuprous cyanide.

A critical examination of the equilibrium diagram of the potassium argentocyanides suggests one or two points of interest in connexion with the well-known volumetric method for titrating cyanides with silver nitrate. The end-point in this method, as is well known, corresponds to the formation of $KAg(CN)_2$. The solubility curve for this compound just fails to reach a point representing a solution in which potassium cyanide and silver cyanide are present in the

same proportions as in the solid. A clear solution is obtained, nevertheless, on adding distilled water to pure $KAg(CN)_2$ at the ordinary temperature, and closely related to this is the fact that all solutions in equilibrium with silver cyanide as solid phase contain potassium cyanide and silver cyanide in the molecular ratio 1 : 1 within the limits of the analytical methods employed. This appears to be of fundamental importance. If the AgCN-curve were on either side of its actual position, Liebig's volumetric method for cyanides could not give the excellent results which it actually does. Moreover, the condition of the silver in solution at the end-point of the titration would seem to be more complicated than is generally assumed. Although the major part is doubtless there as $KAg(CN)_2$ or its ions, some will presumably be present as $KAg_2(CN)_3$ and $K_3Ag(CN)_4$ and the corresponding ions.

(c) *The System Potassium Cyanide–Aurous Cyanide–Water.*

In his investigations on simple and double cyanides, Rammelsberg (*Pogg. Ann.*, **1837, 42, 133**) showed the formation of a potassium gold cyanide which may have been either the aurocyanide or the auricyanide. It appears that Himly (*Annalen*, 1842, **42**, 157, 337) must be credited with the discovery of potassium aurocyanide, $KAu(CN)_2$.

In the present investigation, the salt $KAu(CN)_2$ was readily obtained by Himly's process and also by crystallisation from a boiling solution of potassium cyanide and excess of aurous cyanide. It was quite permanent in air and unaffected by sunlight.

A phase rule investigation of the system potassium cyanide–aurous cyanide–water has given no indication of the existence of any compounds other than $KAu(CN)_2$.

The results of the analyses of the liquid and moist solid phases in equilibrium are given in Table IV (p. 1673) and plotted in Fig. 3. It will be seen that potassium cyanide has a very small range of existence in contact with solutions containing aurous cyanide. The solubility curves of aurous cyanide and potassium aurocyanide, $KAu(CN)_2$, are the two marked features of the diagram, which indicates the existence only of the one aurocyanide. It is worthy of note that solutions containing between 20 and 41 per cent. of potassium cyanide contain less than 1 per cent. of aurous cyanide. In fact, compared with the ready solubility of the compounds $KCu(CN)_2$ and $KAg(CN)_2$, the small extent to which the corresponding aurocyanide dissolves is remarkable.

The solution with which both aurous cyanide and potassium aurocyanide are in equilibrium at 25° contains potassium cyanide and aurous cyanide in the same proportion as does the aurocyanide

itself. It follows, therefore, that the double salt can be crystallised from pure water without decomposition.

The solubility of aurous cyanide is greatest in the solution just referred to, which contains 4·78 per cent. of potassium cyanide. Doubtless this has some bearing on the fact that gold dissolves most rapidly in potassium cyanide solutions of about this concentration (Maclaurin, J., 1893, **63**, 724).

(d) *The System Potassium Cyanide–Thallous Cyanide–Water.*

That thallium forms complex cyanides such as $TlAg(CN)_2$ and $Tl_3Co(CN)_6$, in which it functions as an alkali metal, is well known, but much uncertainty is shown in chemical literature as to whether or not complex thallocyanides exist.

Friend ("Text-book of Inorganic Chemistry," 1917, IV, 199) states that thallous cyanide dissolves in aqueous potassium cyanide, forming soluble potassium thallium cyanide, whilst according to Roscoe and Schorlemmer ("Treatise on Chemistry," 1923, II, Pt. 1, 787) thallous cyanide is readily soluble in potassium cyanide and forms crystalline double cyanides. Main Smith (*Chem. and Ind.*, 1923, **42**, 850), however, states that univalent thallium is apparently devoid of co-ordination properties.

In the present investigation, it was found that, although thallous cyanide is readily soluble in hot aqueous potassium cyanide, it is deposited again unchanged on cooling. It behaves in precisely the same manner with hot water and in this way no indication was obtained of the existence of any potassium thallocyanides.

A phase rule study of the three-component system potassium cyanide–thallous cyanide–water at 25° revealed the existence of the thallocyanide $KTl(CN)_2$.

The results of the analyses of the liquid and moist solid phases in equilibrium are given in Table V on p. 1674 and plotted in Fig. 4.

As the solutions in equilibrium with potassium thallocyanide have such a small range of concentration, it was a matter of considerable difficulty to obtain results in this region. The thallocyanide forms colourless, rectangular prisms which can be readily distinguished from crystals of either potassium cyanide or thallous cyanide.

An attempt was made by washing with aqueous alcohol to separate potassium thallocyanide from a mixture of this compound and potassium cyanide which was obtained as a solid phase in the course of the investigation. An analysis of the crystals so obtained indicated the salt $KTl(CN)_2$, although the separation was far from complete [Found: KCN = 25·02; TlCN = 69·56. $KTl(CN)_2$ requires KCN = 22·06; TlCN = 77·94 per cent.].

The diagrams show that thallous cyanide is stable in contact with solutions of widely different concentrations. The salt $KTl(CN)_2$ has a very small range of existence, which is shown on a larger scale in Fig. 4A. Two of the "tie-lines" in this region do not run to the point for pure $KTl(CN)_2$, but this may be due to the fact that equilibrium had not been attained.

Complex Cyanides and the Electronic Theory of Valency.

Applying the electronic theory of valency to the complex cyanides considered in this paper, it is found that the anhydrous salts $K_3Cu(CN)_4$ and $K_3Ag(CN)_4$ have 18 electrons in the outer shell of the copper and of the silver atom. This, according to Langmuir, should represent a condition of maximum stability, and in view of this fact, it is rather surprising that the anhydrous argentocyanide was not obtained, but only the salt with 1 mol. of water. It is possible that in the case of the hydrated tripotassium salts the water molecule is associated with the potassium.

In a compound $K_3Au(CN)_4$, presumably there would be 32 electrons in the outer shell of the gold atom. It might have been expected, therefore, that such a compound would be obtained readily, but the phase rule investigation showed that it does not exist at 25°.

A glance at Figs. 1—4 shows that there is a very close similarity between the copper and silver systems, which are, however, strikingly different from those of gold and thallium.

Experimental.

Cuprocyanides.

Cuprous cyanide was obtained as a cream-white, micro-crystalline powder by adding hot aqueous potassium cyanide to a hot solution of copper sulphate until the cuprous cyanide which separated was completely redissolved, removing the paracyanogen formed, adding dilute sulphuric acid to the filtrate, washing the precipitate with cold water, and drying it in the air.

The best commercial potassium cyanide was used, but it contained as much as 3 per cent. of potassium hydroxide. An attempt to neutralise this with hydrocyanic acid was not successful, a large amount of brown substance, possibly paracyanogen, being deposited. The use of potassium cyanide containing hydroxide meant that in some cases small amounts of potassium hydroxide were introduced into the system under investigation, thus causing a slight uncertainty as to the exact compositions of the solutions. Eventually this difficulty was surmounted in large measure by preparing the

mixtures from the double salts where possible, as these could be obtained practically free from hydroxide and thus the presence of hydroxide only affected the relatively small portion of the curve representing mixtures containing an excess of potassium cyanide.

Investigation showed that the presence of potassium hydroxide lowers the solubility of potassium cyanide in water, but the total potassium in solution remains almost constant (Table I).

TABLE I.

Showing the effect of addition of potassium hydroxide on the solubility of potassium cyanide in water at 25°.

	100 Grams of solution contain					
KCN	41·56	41·67	38·92	34·72	33·58	26·39
KOH (in terms of KCN)	0·11	0·69	3·30	7·39	8·96	16·29
Total KCN + KOH	41·67	42·36	42·22	42·11	42·54	42·68

No published figures for the solubility of potassium cyanide were found and the value taken in this investigation is 41·7.

Various mixtures of potassium and cuprous cyanides and water were made up in wax bottles so that liquid and solid phases were present. In order to eliminate any errors due to oxidation, the water used was boiled and cooled in a current of coal gas washed by passing through solutions of lead acetate and sodium hydroxide, and before the bottles were sealed the air was replaced by coal gas. The bottles were then rotated in a thermostat at 25° for several days. After 4 or 5 days, when equilibrium was attained, the mixtures were examined and analysed. When the solid phase present was $KCu(CN)_2$ or $KCu_2(CN)_3,H_2O$, the bottles were opened after 2 days, the solid was thoroughly ground, and the bottles were replaced in the thermostat for a further 3 or 4 days. This precaution appeared necessary, as the solid phase crystallised out on nuclei of cuprous cyanide and so retarded the attainment of equilibrium. By making up the mixtures with a potassium cuprocyanide and either potassium cyanide or cuprous cyanide equilibrium was more readily attained.

The liquid to be analysed was sucked into a small weighed conical flask through an asbestos filter jacketed with water at 25°. In this way, filtration was rapid and no cooling effects were introduced. After being weighed, the clear filtrate was made up to a definite volume (generally 100 c.c.) with water. The moist solid was roughly pressed on filter paper and transferred to a small weighing bottle.

The methods of analysis of the liquid and moist solid phases were essentially the same. Standard (0·5*N*) sulphuric acid was added in excess of that required to precipitate the cuprous cyanide

completely. After 12 hours, the cuprous cyanide was collected on a weighed Gooch crucible and dried in an oven for several hours at 120° and finally at 130° until a constant weight was obtained. The filtrate was titrated against standard (0·5*N*) sodium hydroxide and methyl-orange, and the total alkalinity was calculated from the excess of sulphuric acid thus determined. When potassium hydroxide was present owing to potassium cyanide having been used in preparing the mixtures, a separate determination of potassium cyanide was necessary. This was made by distilling the substance with the amount of standard sulphuric acid which the acid titration had shown to be necessary to decompose the complex. The distillate of hydrocyanic acid was received in an alkaline solution and titrated against 0·1*N*-silver nitrate solution in presence of ammonia and potassium iodide. If more than the calculated amount of acid was used for the decomposition, high results were obtained and the cuprous cyanide might redissolve. In such cases the hydrocyanic acid found in the distillate was partly derived from the cuprous cyanide. Estimating the total cyanide in the complex cyanides by distillation was untrustworthy because the strength of acid required to complete the hydrolysis was such that some formation of carbon monoxide invariably occurred. Occasionally the copper was estimated iodometrically after the complex had been destroyed by warming with sulphuric acid containing a few drops of nitric acid. With the stronger solutions trustworthy results were thus obtained, but when small amounts of copper were present the end-point was indefinite.

The solids are all colourless, and of fairly distinctive appearance when examined under the microscope. The salt $K_3Cu(CN)_4,H_2O$ forms large rhombohedra, $K_3Cu(CN)_4$ has a more prismatic tendency, $KCu(CN)_2$ usually gives plates of hexagonal form and needles, whilst $KCu_2(CN)_3,H_2O$ forms minute, monoclinic scales.

The compounds $KCu(CN)_2$ and $KCu_2(CN)_3,H_2O$ can be obtained almost free from mother-liquor by washing with alcohol—a fortunate matter, in the latter case, for the conclusive demonstration that the salt is hydrated [Found: KCN = 24·22; CuCN = 68·48. $KCu_2(CN)_3,H_2O$ requires KCN = 24·83; CuCN = 68·32; H_2O = 6·85 per cent.]. $K_3Cu(CN)_4$ and its hydrate are appreciably soluble in alcohol and it was almost impossible to separate the pure salt from the moist solid phase.

The nature of the solid phase separating from the liquid could readily be inferred. The colourless tripotassium salt always separated from a liquid of a yellow colour, even when it was prepared from potassium and cuprous cyanides; the cause of this yellow colour, which disappeared on acidification, was not dis-

covered. The compounds $KCu(CN)_2$ and $KCu_2(CN)_3,H_2O$ separated from colourless solutions; in the latter case, crystals separated from the liquid phase very readily on cooling, showing that the solubility was considerably affected by temperature; such separation did not occur with $KCu(CN)_2$.

The hydrate $KCu_2(CN)_3,H_2O$ was prepared in small quantity by digesting an excess of cuprous cyanide with a boiling 10 per cent. solution of potassium cyanide for some time. On decanting, the salt immediately crystallised from the solution, and on concentrating the mother-liquor, the salt $KCu(CN)_2$ was deposited and eventually $K_3Cu(CN)_4$. It was often a matter of extreme difficulty to free the compounds from excess of potassium cyanide, although $KCu(CN)_2$ was obtained fairly pure in this manner [Found: KCN = 43·79; CuCN = 56·36. $KCu(CN)_2$ requires KCN = 42·09; CuCN = 57·91 per cent.].

The tripotassium salt was readily prepared by evaporating a solution containing potassium and cuprous cyanides in the proportion demanded by the formula $K_3Cu(CN)_4$. After filtration and washing with alcohol, large, colourless rhombohedra were often deposited from the alcoholic mother-liquor on standing. Analysis of these crystals, which are quite permanent in air, gave fairly good agreement with the formula $K_3Cu(CN)_4,H_2O$ [Found: KCN = 65·56; CuCN = 29·86. $K_3Cu(CN)_4,H_2O$ requires KCN = 64·47; CuCN = 29·57; H_2O = 5·94 per cent.].

Violet crystals together with green needles were obtained by keeping the salt $KCu_3(CN)_3,H_2O$ in contact with strong ammonia solution for several weeks. In similar circumstances, $KCu(CN)_2$ gave dark green plates, and the tripotassium salt was apparently unchanged.

Argentocyanides.

Silver cyanide was prepared from silver nitrate by a method similar to that employed in the case of cuprous cyanide; cold solutions were used and the operations were for the most part carried out in the dark, as the cyanide turned violet on exposure to sunlight.

The procedure followed in the examination of the silver cyanide system was, in general, that of the previous system.

The method of estimating silver by weighing it as silver cyanide was untrustworthy when applied to mixtures containing a high percentage of silver, yielding results 1 to 3 per cent. too low; * for such mixtures, therefore, the complex in a separate sample of the liquid or solid was decomposed by boiling with fairly concentrated nitric acid, and the silver weighed as chloride in the usual manner.

* This seems to be due to the appreciable stability of the argentocyanic acids.

TABLE II.

Composition of Phases in the System KCN–CuCN–H_2O *at* 25°.

Liquid phase. KCN %	Liquid phase. CuCN %	Moist solid phase. KCN %	Moist solid phase. CuCN %
Solid phase : KCN.			
41·7	0·00	—	—
40·53	2·16	92·95	trace
40·31	4·20	89·66	trace
Solid phase : $K_3Cu(CN)_4$.			
41·70	5·84	63·14	29·00
35·96	10·86	65·82	30·15
33·86	15·30	63·06	29·60
Solid phase : $K_3Cu(CN)_4,H_2O$.			
41·94	6·13	65·16	29·83
36·24	12·92	64·29	30·63
34·82	18·47	69·85	29·11
35·28	22·52	59·96	29·13
Solid phase : $KCu(CN)_2$.			
34·77	22·59	41·02	53·54
22·32	14·71	41·46	54·76
19·95	13·78	40·73	50·76
12·10	8·84	38·38	50·23
Solid phase : $KCu_2(CN)_3,H_2O$.			
9·97	7·52	23·42	65·61
6·05	3·93	24·08	62·04
6·03	3·88	24·86	61·82
4·21	1·87	26·59	65·12
3·27	1·68	23·10	62·33
1·34	0·60	22·75	63·49
Solid phase : $KCu_2(CN)_3,H_2O$ + CuCN			
0·46 *	trace	19·38	59·27
0·54	trace	14·82	59·82
0·39	trace	13·97	62·63
0·25	trace	12·39	63·20
0·37	trace	10·63	56·61
0·52	trace	9·56	59·10
Solid phase : CuCN.			
trace	trace	trace	67·23

* The small differences shown above in the KCN column (liquid phase) are doubtless due to analytical difficulties. All six experiments undoubtedly represent a solution saturated with respect to both $KCu_2(CN)_3,H_2O$ and CuCN and give the point of intersection of the solubility curves of these two compounds.

With this exception the same methods of analysis were employed as for the cuprous compounds.

The moist solid phases were of course contaminated with mother-liquor, and an attempt was made to remove this by washing with alcohol. Although this was not very successful, analyses performed on the dry products thus obtained left little doubt that the compounds $K_3Ag(CN)_4$ and $KAg_2(CN)_3$ were hydrated, thus confirming the indications given by the triangular diagram [Found: KCN = 58·30; AgCN = 37·17. $K_3Ag(CN)_4,H_2O$ requires KCN = 56·25; AgCN = 38·56; H_2O = 5·19 per cent. Found: KCN = 21·04; AgCN = 75·07. $KAg_2(CN)_3,H_2O$ requires KCN = 18·54; AgCN = 76·33; H_2O = 5·13 per cent.].

As was the case with the cuprocyanides, the compound $K_3Ag(CN)_4,H_2O$ separated (as a white, crystalline powder) from a yellow solution, the other salts from colourless solutions, and minute needles of the compound $KAg_2(CN)_3,H_2O$ were readily deposited in the separated liquid phase on cooling to room temperature.

The solubility curve of the compound $K_3Ag(CN)_4,H_2O$ passes through a point representing a solution in which the ratio KCN : AgCN

is the same as in the solid salt. This salt, therefore, can be recrystallised from water, as can the corresponding cuprous compound.

The salt $KAg(CN)_2$ was obtained fairly pure, in colourless crystals, by adding excess of silver cyanide to a boiling aqueous 20 per cent. solution of potassium cyanide, and allowing the decanted solution to cool [Found: KCN = 32·79; AgCN = 67·22. $KAg(CN)_2$ requires KCN = 32·72; AgCN = 67·28 per cent.]. Under the microscope the crystals appeared broken, but some hexagonal plates were detected. This salt was quite stable in air, and, contrary to the statement of Glassford and Napier, it was not affected by light.

On evaporating a solution containing potassium and silver cyanides in the ratio 3 : 1, the compound $K_3Ag(CN)_4,H_2O$ was readily obtained in large quantity as large colourless tabular prisms. It is stable in the air and unaffected by light [Found: KCN = 56·28; AgCN = 38·58 per cent.].

TABLE III.

Composition of Phases in the System KCN–AgCN–H_2O *at* 25°.

Liquid phase.		Moist solid phase.		Liquid phase.		Moist solid phase.	
KCN %.	AgCN %.	KCN %.	AgCN %.	KCN %.	AgCN %.	KCN %.	AgCN %.
Solid phase : KCN.				Solid phase : $KAg_2(CN)_3,H_2O$.			
41·7	0·00	—	—	8·05	15·76	18·06	71·26
40·77	6·52	91·63	trace	8·93	17·73	17·48	70·73
39·91	8·14	92·33	trace				
40·24	10·93	99·04	trace	Solid phase : AgCN.			
Solid phase : $K_3Ag(CN)_4,H_2O$.				6·75	13·53	1·74	77·12
40·44	13·71	61·45	36·48	2·36	4·42	0·95	80·63
37·76	18·92	56·18	37·93	1·64	3·27	0·56	79·48
35·19	25·18	57·44	39·05	1·26	2·31	1·06	81·18
Solid Phase : $KAg(CN)_2$.				0·17	trace	trace	75·10
28·43	26·37	33·58	64·99	nil	0·000029*	—	—
26·67	24·71	30·20	58·41				
20·14	21·66	30·26	63·94				
8·56	16·11	31·69	64·63				

* Bodländer and Lucas, *Z. anorg. Chem.*, 1904, **41**, 192.

Aurocyanides.

Aurous cyanide was readily obtained as a glistening, lemon-yellow, crystalline powder by boiling an aqueous solution of potassium aurocyanide with 2*N*-hydrochloric acid, and, after filtration with the aid of the pump, was washed with cold water and dried on a porous tile.

Mixtures for the solubility determinations were made up as in previous cases, the subsequent procedure being also similar up to the point of the actual analyses.

With slight modification Himly's procedure was adopted for the analysis of the liquid and moist solid phases. The weighed solid

or liquid was boiled with 2*N*-hydrochloric acid until the evolution of hydrocyanic acid ceased, then, after cooling, the precipitated aurous cyanide was collected on a weighed Gooch crucible and heated to constant weight at 120—130°. The potassium in the filtrate was estimated as sulphate.

Direct titration of the potassium with acid gave unsatisfactory results owing to the strength and stability of aurocyanic acid. Any potassium hydroxide present could not be estimated directly on this account. Its amount, however, could be calculated from that known to be present in the potassium cyanide solutions used in preparing the various mixtures. The figures for KCN given in the table have been corrected for the hydroxide thus found.

An attempt to remove the mother-liquor from the moist solid phases by washing with alcohol was not very successful, but an analysis of the product showed that the compound was not hydrated [Found: KCN = 22·76; AuCN = 75·68. $KAu(CN)_2$ requires KCN = 22·58; AuCN = 77·42 per cent.].

As in the previous investigations, it was found that the aurocyanide separated from a yellow solution when excess of potassium cyanide was present, whilst colourless solutions were obtained when the potassium cyanide present was not in excess of that stoicheiometrically required for the salt $KAu(CN)_2$. The fact that crystals were readily deposited on cooling the filtered liquid showed that the solubility of the salt is largely affected by temperature.

TABLE IV.

Composition of Phases in the System KCN–AuCN–H_2O *at* 25°.

Liquid phase.		Moist solid phase.		Liquid phase.		Moist solid phase.	
KCN	AuCN	KCN	AuCN	KCN	AuCN	KCN	AuCN
%	%	%	%	%	%	%	%
Solid phase : KCN.				9·66	2·97	22·76	75·68
41·7	0·00	—	—	7·02	8·34	25·70	72·95
42·02	trace	91·23	trace	5·19	11·02	21·60	73·00
Solid phase : KCN+$KAu(CN)_2$.				Solid phase : $KAu(CN)_2$+AuCN.			
41·98	0·17	30·09	65·23	4·78	15·47	17·58	77·55
Solid phase : $KAu(CN)_2$.				Solid phase : AuCN.			
38·98	0·35	25·10	68·69				
24·04	0·76	22·90	73·00	2·60	7·27	0·73	88·76
23·79	0·27	23·52	70·15	2·32	7·32	0·63	65·00
13·70	2·55	22·63	73·84	2·37	6·12	Not analysed.	

Thallocyanides.

Thallous cyanide was prepared by admixture of hot solutions of thallous nitrate and potassium cyanide and allowing to crystallise. The white hexagonal plates of thallous cyanide thus obtained were purified by recrystallisation from hot water.

TABLE V.

Composition of Phases in the System KCN–TlCN–H_2O *at* 25°.

Liquid phase.		Moist solid phase.		Liquid phase.		Moist solid phase.	
KCN %	TlCN %	KCN %	TlCN %	KCN %	TlCN %	KCN %	TlCN %
Solid phase : KCN.				Solid phase : TlCN.			
41·7	0·00	—	—	36·00	4·99	4·06	87·38
40·83	0·71	90·33	0·24	35·27	4·98	3·32	88·99
39·76	1·65	86·68	0·70	34·45	4·91	3·34	89·69
				34·36	4·90	2·90	90·66
				34·09	4·96	3·49	90·13
Solid phase : KCN+$KTl(CN)_2$.				31·25	4·46	2·60	90·45
37·35	3·17	59·57	30·24	30·21	5·00	3·76	89·40
36·69	3·17	54·01	24·69	28·07	4·47	4·12	91·75
				21·00	4·36	2·47	85·48
				14·75	5·46	1·19	92·88
Solid phase : $KTl(CN)_2$.				9·12	7·17	0·96	91·00
37·50	3·11	26·40	57·78	0·51	16·20	trace	89·89
36·47	4·16	25·83	68·88	0·34	16·12	trace	91·37
36·52	4·12	31·79	62·23	0·00	16·53	0·00	85·60
35·93	5·78	22·10	70·82	0·00	16·49	0·00	94·89

Abegg ("Handbuch der anorganische Chemie," 1906, III, 425) gives values for the solubility of thallous cyanide in water at three temperatures; by interpolation, at 25° 100 grams of solution would contain 18·9 grams of thallous cyanide. According to Fronmüller (*Ber.*, 1878, **11**, 92), the solubility at 28·5° is 14·4 grams in 100 grams solution.

In this investigation, it was found that at 25°, 100 grams of solution contain 16·5 grams of thallous cyanide and this value has been employed.

The mixtures for solubility determinations were made up as in previous cases and shaken at 25° until equilibrium was attained.

The liquid and moist solid phases were separated by the apparatus used previously and the methods of analysis adopted were the same for both phases.

The weighed liquid or moist solid was warmed with dilute sulphuric acid to decompose any complex which might have been formed, then, the solution having been made ammoniacal, the thallium was precipitated as sulphide by means of hydrogen sulphide. The black precipitate was filtered off, dissolved in nitric acid, the solution made alkaline with sodium carbonate, and thallous iodide precipitated by addition of potassium iodide. After standing, the thallous iodide was collected on a weighed Gooch crucible and dried to constant weight at 120—130°.

The potassium remaining in the filtrate from the thallous sulphide was weighed as sulphate.

The amount of potassium present as hydroxide was calculated,

and allowance for it made, in the same way as in the investigation of the last system.

As found previously, yellow solutions were obtained with mixtures containing a high percentage of potassium cyanide.

Summary.

A phase rule investigation of the systems (*a*) KCN–CuCN–H_2O, (*b*) KCN–AgCN–H_2O, (*c*) KCN–AuCN–H_2O, and (*d*) KCN–TlCN–H_2O has been made at 25°. This has shown the conditions of concentration under which various double cyanides can be obtained at this temperature. Several of these compounds were already well known, others have been prepared for the first time.

Various points of interest arising out of the results obtained have been discussed.

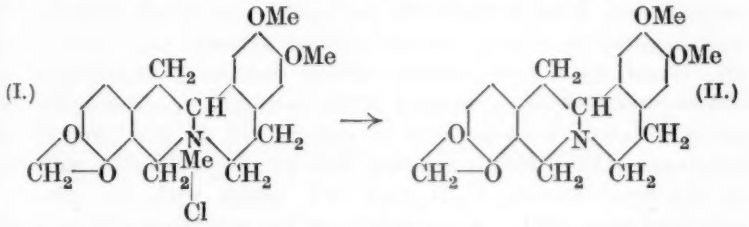
We wish to thank the Department of Scientific and Industrial Research for a maintenance grant awarded to one of us (A. S. C.), and the Chemical Society for a grant which helped to defray the expense of the work. We are also indebted to Messrs. R. A. Chell and H. C. Cockroft for some preliminary work in connexion with the cuprous cyanide system.

UNIVERSITY COLLEGE, READING. [*Received, March 22nd,* 1924.]

CCXVIII.—ψ-epi*Berberine.*

By JOHANNES SYBRANDT BUCK and WILLIAM HENRY PERKIN, junr.

*epi*BERBERINE and its derivatives have so far only been obtained from cryptopine by the removal of the methyl group attached to nitrogen (J., 1918, **113**, 492). This interesting change is best accomplished by heating *iso*dihydrocryptopine α-chloride (I) at 270°, when it is decomposed with elimination of methyl chloride and formation of tetrahydro*epi*berberine (II., *loc. cit.*, p. 510).*

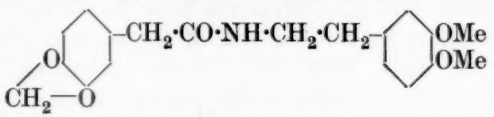


The *epi*berberine salts, like those of berberine, are bright yellow and the characteristic decomposition of berberinium chloride into oxyberberine and dihydroberberine on treatment with alkali has

* Compare footnote, p. 1690.

its parallel in the conversion of *epi*berberinium chloride into oxy-*epi*berberine and dihydro*epi*berberine under the same conditions (*loc. cit.*, p. 500). During the course of further experiments on *epi*berberine, the difficulty of obtaining this substance in any quantity from cryptopine, due mainly to the rarity of this alkaloid but also to the poor yield obtained as the result of the elimination of methyl chloride under the conditions mentioned above, suggested that it would be well worth while to endeavour to prepare this alkaloid synthetically. With this object in view, we decided to make use of a method closely resembling that used by Pictet and Gams (*Ber.*, 1911, **44**, 2480) in their experiments on the synthesis of berberine. Veratraldehyde was condensed with ethyl acetate in presence of sodium, and the resulting dimethoxycinnamic acid reduced to the corresponding dimethoxyphenylpropionic acid, $(MeO)_2C_6H_3\cdot CH_2\cdot CH_2\cdot CO_2H$ (Perkin and Robinson, J., 1907, **91**, 1079). The amide of this acid yielded, on treatment with sodium hypochlorite, homoveratrylamine, $(MeO)_2C_6H_3\cdot CH_2\cdot CH_2\cdot NH_2$ (Decker, *Annalen*, 1913, **395**, 291). On the other hand, piperonal was condensed with hippuric acid and the azlactone hydrolysed to benzoic acid and piperonylpyruvic acid, $CH_2O_2{:}C_6H_3\cdot CH_2\cdot CO\cdot CO_2H$; the latter was then oxidised by hydrogen peroxide to homopiperonylic acid, $CH_2O_2{:}C_6H_3\cdot CH_2\cdot CO_2H$ (Kropp and Decker, *Ber.*, 1909, **42**, 1188; Mauthner, *Annalen*, 1909, **370**, 375).

The first step in the actual synthesis was to condense homopiperonylic chloride with homoveratrylamine and this resulted in the formation of *homopiperonoyl-homoveratrylamine* (III):

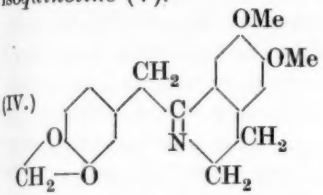
(III.) 

The conversion of this substance into 1-*homopiperonyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*isoquinoline (IV) presented some difficulty, because only a small yield (30 per cent.) was obtained when (III) was digested in boiling xylene with phosphorus pentoxide (Pictet and Gams, *loc. cit.*, p. 2482). When, however, phosphorus oxychloride was employed instead of the pentoxide, condensation took place smoothly with a yield of upwards of 80 per cent. of the substance (IV). This is a strong base yielding colourless salts such as the *hydrochloride*, $C_{19}H_{19}O_4N$,HCl, which with the *picrate* is described on p. 1681. A peculiarity of the substance (IV) is that it is readily oxidised in contact with air with the formation of an interesting base, $C_{19}H_{17}O_5N$, which melts at 151—152°, the investigation of which is in progress.

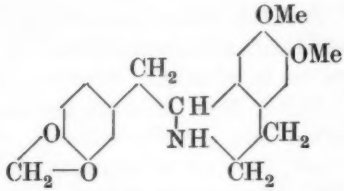
When the substance (IV) is digested with zinc and sulphuric acid,

it is reduced smoothly to 1-*homopiperonyl*-6 : 7-*dimethoxytetrahydroisoquinoline* (V).

(IV.)



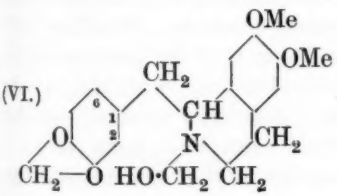
(V.)



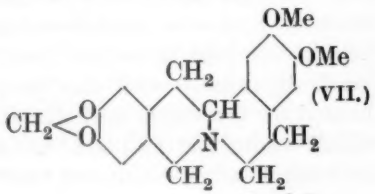
The next step was to condense this substance (V) with methylal, but, although a large number of experiments were made under conditions similar to those recommended by Pictet and Gams (*loc. cit.*, p. 2484), crystalline products could not be isolated either directly or indirectly. When, however, the methyl-alcoholic solution of (V) is treated with formaldehyde, the formyl derivative separates as a gum and this, on warming with hydrochloric acid, is at once converted into the sparingly soluble salt of the tetrahydroalkaloid which it was presumed would prove to be tetrahydro-*epi*berberine (II). Careful examination of the alkaloid obtained by the addition of alkali to the hydrochloride proved conclusively that it is not tetrahydro*epi*berberine. It separates beautifully from methyl alcohol in prismatic needles melting at 160—161°, whereas tetrahydro*epi*berberine melts at 170—171° (compare J., 1918, **113**, 512). Moreover, an intimate mixture of equal quantities of the two substances melted at about 143°. Furthermore, the investigation of the behaviour of the base on oxidation (see below) clearly proved that it could not be tetrahydro*epi*berberine.

A careful examination was made in order to see whether any second substance had been produced, but without success, and therefore it would appear that ring formation, due to the action of hydrochloric acid on the formyl derivative (VI) had proceeded entirely in the one direction. Theoretically there are two ways in which ring formation can occur (compare Pictet and Gams, *loc. cit.*). If the condensation takes place with the aid of the hydrogen atom in position 2, tetrahydro*epi*berberine (II) will be produced, but if, on the other hand, it is the hydrogen in position 6 which takes part in the change the result must be the formation of the isomeric alkaloid—*tetrahydro*-ψ-epi*berberine* (VII).

(VI.)



(VII.)

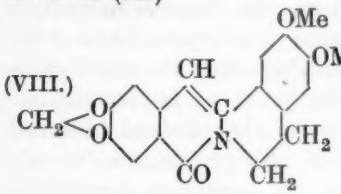


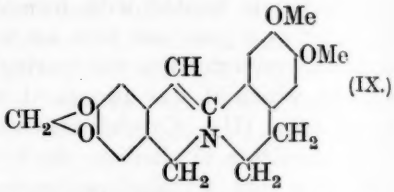
3 N* 2

That the substance actually formed in this condensation is tetrahydro-ψ-*epi*berberine has already been indicated, but conclusive proof that this view is correct is furnished by the careful examination of the substance. When this tetrahydro-derivative is oxidised by iodine in alcoholic solution, it yields ψ-epi*berberinium iodide*, $C_{20}H_{18}O_4NI$, and this, on decomposition with silver chloride, is converted into ψ-epi*berberinium chloride*. This interesting quaternary salt, like all substances of this type, is yellow and readily soluble. It is curious that it exists in three modifications, namely, (i) as $C_{20}H_{18}O_4NCl,4\frac{1}{2}$ aq, (ii) $C_{20}H_{18}O_4NCl,2\frac{1}{2}$ aq, and (iii) as the anhydrous chloride.

But the most characteristic property of this substance is its decomposition into *oxy*-ψ-epi*berberine* (VIII) and *dihydro*-ψ-epi*berberine* (IX)

(VIII.)





(IX.)

on treatment with sodium hydroxide, a reaction exactly analogous to the conversion of *epi*berberinium chloride into oxy*epi*berberine and dihydro*epi*berberine under the same conditions (J., 1918, **113**, 517). Oxy-ψ-*epi*berberine melts at 206°, whereas oxy*epi*berberine melts at 240—241°; on the other hand, dihydro-ψ-*epi*berberine and dihydro*epi*berberine melt almost at the same temperature, namely, at 173° and 172° respectively. The mixture of the two latter melts at 143°.

This description of its properties can only lead to the conclusion that the base obtained from 1-homopiperonyl-6 : 7-dimethoxytetrahydro*iso*quinoline (V) by the action of formaldehyde and hydrochloric acid is tetrahydro-ψ-*epi*berberine and not tetrahydro-*epi*berberine.

EXPERIMENTAL.

Veratraldehyde.—Perkin and Robinson (J., 1907, **91**, 1079) describe the preparation of this substance from vanillin and methyl sulphate and use methyl alcohol as the solvent, but the methylation may also be carried out in aqueous solution. Vanillin (120 gms.), dissolved in sodium hydroxide (64 c.c. of 10 per cent.), is gradually mixed with methyl sulphate (100 c.c.) and the whole heated on the steam-bath for an hour. A further quantity of the alkali (about 350 c.c.) is added as well as methyl sulphate (60 c.c.) and the heating continued, care being taken that the mixture is

just alkaline during the whole operation. The product is extracted with ether and the ether evaporated, when veratraldehyde remains in amount approximately equal to that of the vanillin taken. This aldehyde was converted into 3 : 4-dimethoxycinnamic acid by interaction with ethyl acetate and sodium and reduced by sodium amalgam to 3 : 4-dimethyloxyphenylpropionic acid (Perkin and Robinson, *loc. cit.*, p. 1080).

3 : 4-*Dimethoxyphenylpropionamide*, $(MeO)_2C_6H_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$. —Some difficulty was met with in developing a process for the preparation of this substance in good yield. The conversion of the acid into the acid chloride by means of phosphorus pentachloride, followed by interaction with ammonia, proved unsuitable in the case of large quantities of material (cf. Pictet and Finkelstein, *Ber.*, 1909, **42**, 1985). Other attempts to prepare the acid chloride with the aid of thionyl chloride and to treat this substance, or the corresponding ester, with ammonia under a variety of conditions did not give good results.

Ultimately, the following method, based on that recommended by Decker (*Annalen*, 1913, **395**, 290) for the preparation of piperonylacetamide, was adopted with success. The carefully dried acid is gradually heated at 220—230° while a stream of dry ammonia is passed for 2 hours. After cooling, the syrup is dissolved in hot benzene, from which the amide rapidly separates as a granular mass melting, after a second crystallisation, at 121°.

Homoveratrylamine, $(MeO)_2C_6H_3 \cdot CH_2 \cdot CH_2 \cdot NH_2$.—Pictet and Finkelstein (*loc. cit.*, p. 1986) obtained this substance from 3 : 4-dimethoxyphenylpropionamide by interaction with excess of sodium hypobromite (cf. Graebe, *Ber.*, 1902, **35**, 2747). Decker (*loc. cit.*, p. 291) recommends sodium hypochlorite for purposes of this kind, and we have adopted this reagent in the present case. A solution of sodium hypochlorite is prepared by passing the chlorine generated from potassium permanganate (6 gms.) and hydrochloric acid into cold sodium hydroxide (230 c.c. of 10 per cent.). The amide (20 gms.) dissolves in this solution on warming gently and the temperature is then gradually raised to 70—75° and kept at this for an hour, during which a layer of oil separates. Solid potassium hydroxide (60 gms.) is now added, the whole heated at 80° for a few minutes, left to cool gradually during 2 hours, and extracted three times with benzene. After drying over solid potash and evaporation of the solvent, homoveratrylamine remains as a pale yellow oil, the yield being about 70 per cent. of theory.

The *homopiperonylic acid*, $CH_2{:}O_2{:}C_6H_3 \cdot CH_2 \cdot CO_2H$, required as one component in the synthesis described in the next section was

prepared from the so-called azlactone, obtained by condensing piperonal with hippuric acid (Kropp and Decker, *Ber.*, 1909, **42**, 1188), by hydrolysing it with alkali to benzoic acid and piperonylpyruvic acid, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$. The benzoic acid was separated by passing sulphur dioxide into the alkaline solution, removed by filtration, and the filtrate, containing the bisulphite derivative of the pyruvic acid, heated on the steam-bath with excess of strong hydrochloric acid. The pyruvic acid was collected and oxidised in alkaline solution with hydrogen peroxide (compare Mauthner, *Annalen*, 1909, **370**, 375), when, on acidifying, pure homopiperonylic acid (m. p. 127°) separated in good yield.

Homopiperonoyl-homoveratrylamine (III).

There are two methods which may be conveniently used for preparing this substance. The first, which has the advantage of not requiring great purity of the initial material, consists in heating an equimolecular mixture of homopiperonylic acid and homoveratrylamine at 180—200° for an hour and crystallising the product from alcohol. The condensation product was, however, usually prepared in the following manner: Homopiperonylic acid (8 gms.) is dissolved in a little chloroform, and thionyl chloride (4·2 c.c.) added to the solution. After boiling gently for 45 minutes, the chloroform is distilled off and the yellow oil added in portions to an emulsion of homoveratrylamine (8·0 gms.) in potassium hydroxide (50 c.c. of 10 per cent.), the mixture being vigorously shaken during the addition. The condensation product rapidly separates in nodules and is purified by crystallisation from alcohol (Found: C = 66·2; H = 6·0; N = 4·1. $C_{19}H_{21}O_5N$ requires C = 66·5; H = 6·1; N = 4·1 per cent.). *Homopiperonoyl-homoveratrylamine* separates from alcohol in aggregates of tufted needles but from benzene in small, irregular needles and melts at 130—131°. It dissolves readily in alcohol, less readily in benzene, is sparingly soluble in ether, and almost insoluble in petroleum. It dissolves in hot dilute hydrochloric acid and separates unchanged on cooling.

1-*Homopiperonyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*isoquinoline (IV).

Homopiperonoyl-homoveratrylamine (10 gms.), phosphorus oxychloride (20 c.c.), and toluene (50 c.c.) are boiled in a reflux apparatus, when interaction commences at once and is complete in 1½ hours. The brownish-yellow product contains an oil in suspension and, on addition of light petroleum, this is completely precipitated. After decanting the supernatant liquid, the oil soon solidifies and is stirred with alcohol, when an almost colourless, granular mass of a phosphate is obtained which may be readily recrystallised from alcohol.

The phosphate is warmed with alcohol and aqueous sodium hydroxide until a clear, almost colourless solution is obtained. On precipitation with water and scratching vigorously, a colourless mass of felted needles of the dihydro*iso*quinoline separates in a yield of upwards of 80 per cent. of theory. This substance cannot be recrystallised in the usual way from solvents, since it is readily oxidised in contact with air to the substance $C_{19}H_{17}O_5N$, (m. p. 152°, p. 1676). It may, however, be purified by rapidly precipitating a faintly alkaline aqueous alcoholic solution, prepared from the recrystallised phosphate, with water. When pure and dry, it is stable in the air (Found : C = 70·0; H = 5·8. $C_{19}H_{19}O_4N$ requires C = 70·1; H = 5·8 per cent.). *Homopiperonyldimethoxydihydroisoquinoline* is readily soluble in alcohol or benzene, moderately so in ether or light petroleum. It dissolves in dilute sulphuric or hydrochloric acid to a colourless solution, but rapidly decomposes on warming with dilute nitric acid, yielding a yellow to brown solution with the escape of nitrous fumes. It dissolves in cold concentrated sulphuric acid to a dull, not very intense emerald-green and, on the addition of a crystal of potassium nitrate, the colour becomes an intense reddish-violet. When boiled with acetic anhydride, the yellow solution first formed becomes a deep green.

The *hydrochloride* was prepared by dissolving the base in warm alcohol and adding aqueous hydrochloric acid, when it separated as a felted mass of colourless, slender needles (Found : C = 62·7; H = 5·7. $C_{19}H_{19}O_4N$,HCl requires C = 63·1; H = 5·5 per cent.). This hydrochloride is readily soluble in warm water and may be crystallised from dilute hydrochloric acid. It melts at 200° with frothing, becoming yellow.

The *picrate* was prepared by dissolving the base in alcoholic acetic acid and adding alcoholic picric acid, when it separated as tufts of long, sword-like needles of a bright canary-yellow colour (Found : C = 54·3; H = 4·1. $C_{19}H_{19}O_4N$,$C_6H_3O_7N_3$ requires C = 54·2; H = 4·1 per cent.). It melts at 197° and is somewhat soluble in warm water, sparingly soluble in alcohol, and dissolves readily in acetic acid.

1-*Homopiperonyl*-6 : 7-*dimethoxytetrahydroisoquinoline* (V).

Homopiperonyldimethoxydihydro*iso*quinoline is dissolved in excess of hot dilute (*N*/2) sulphuric acid, mixed with a few drops of copper sulphate, a considerable excess of zinc powder (99 per cent.) is added, and the whole heated on the water-bath for 2 hours with frequent shaking. A sparingly soluble sulphate separates and this is collected, decomposed with sodium hydroxide, and the base extracted with ether. On evaporating the ether, the base

soon solidifies and is crystallised from light petroleum, from which it separates in jagged, irregular plates, m. p. 96° (Found: C = 69·6; H = 6·5. $C_{19}H_{21}O_4N$ requires C = 69·7; H = 6·4 per cent.).

Homopiperonyldimethoxytetrahydroisoquinoline is readily soluble in the usual media and is a strong base which dissolves readily in dilute acids. It dissolves in concentrated sulphuric acid to a greenish-brown solution and has a slightly bitter and metallic taste. The *hydrochloride* and *sulphate* are colourless, crystalline substances rather sparingly soluble in cold water.

Tetrahydro-ψ-epiberberine (VII).

In the first attempts to convert homopiperonyldimethoxytetrahydro*iso*quinoline into tetrahydro-ψ-*epi*berberine, the base was treated with methylal and hydrochloric acid exactly under the conditions recommended by Pictet and Gams in their experiments on the conversion of veratrylnorhydrastinine into tetrahydroberberine (*loc. cit.*, p. 2484). The product, after treatment with alkali, consisted of high-melting, amorphous substances and gummy material and we were unable to isolate from it even traces of the tetrahydro-alkaloid. When, however, the methylal was replaced by formaldehyde, excellent results were achieved. The tetrahydro*iso*quinoline (5 gms.), dissolved in methyl alcohol (30 c.c.), was well mixed with sodium bicarbonate (5 gms.) and then formaldehyde (10 c.c. of 40 per cent.) gradually added as well as, from time to time, sufficient methyl alcohol to keep the solution always clear. After the mixture had been warmed for a few minutes on the steam-bath, water was added together with some salt, when a gum separated. This was thoroughly washed with cold water, dissolved in warm concentrated hydrochloric acid, and heated on the steam-bath for a few minutes, when, on cooling, the hydrochloride of tetrahydro-ψ-*epi*berberine separated in needles and was collected and recrystallised from hot dilute hydrochloric acid. The hydrochloride was then decomposed by adding potassium carbonate to the aqueous solution, and the base recrystallised from methyl alcohol (Found: C = 70·8; H = 6·1; N = 4·1. $C_{20}H_{21}O_4N$ requires C = 70·8; H = 6·2; N = 4·1 per cent.).

Tetrahydro-ψ-epiberberine melts at 160—161° and crystallises from methyl alcohol in dense aggregates of jagged, prismatic needles which, under the microscope, have a curious fern-like appearance. Although very similar in appearance and properties to tetrahydro-*epi*berberine (m. p. 170—171°, J., 1918, **113**, 510), there can be no question of identity, since a mixture of the two substances melts at about 140—145°. It dissolves readily in chloroform, is moderately soluble in alcohol or benzene, but sparingly soluble in light

petroleum. It is a strong base, dissolving readily in dilute acids and yielding well-crystallised salts. The *hydrochloride* is moderately soluble in boiling water, very much less soluble in the cold, and very sparingly soluble in cold dilute hydrochloric acid.

The *picrate* separates from an alcoholic solution of the base and picric acid as a finely crystalline, bright yellow precipitate. It dissolves in hot glacial acetic acid, is somewhat soluble in hot alcohol, but only very sparingly soluble in hot water, and melts at 149—150° with frothing and blackening (Found: C = 54·6; H = 4·6. $C_{20}H_{21}O_4N,C_6H_3O_7N_3$ requires C = 54·7; H = 4·2 per cent.).

Very careful search was made in all the mother-liquors for traces of tetrahydro*epi*berberine, but without success.

The ψ-epiBerberinium Salts.

ψ-epi*Berberinium Iodide.*—Tetrahydro-ψ-*epi*berberine, dissolved in the minimum of boiling alcohol, is mixed with anhydrous sodium acetate, and an alcoholic solution of iodine is slowly added until a permanent coloration remains, the whole being heated on the steam-bath during the addition. A pale brown, granular precipitate of the periodide separates and this is collected, washed well, suspended in hot water, and decomposed by the addition of aqueous sulphurous acid. The pale yellow, granular iodide is collected and recrystallised from boiling water, in which it is very sparingly soluble and from which it separates as a pale yellow, crystalline precipitate. Under the microscope, this is seen to be quite homogeneous and to consist of glistening, slender, rhombic prisms (Found: C = 52·0; H = 4·0. $C_{20}H_{18}O_4NI$ requires C = 51·8; H = 3·9 per cent.). ψ-epi*Berberinium iodide* melts at about 303° with frothing and blackening and, although so sparingly soluble in water, has an intensely bitter taste. It colours concentrated sulphuric acid maroon and, on the addition of a crystal of potassium nitrate, a brilliant green is produced.

ψ-epi*Berberinium Chloride.*—This substance is readily obtained when the iodide is digested, in aqueous suspension, with excess of silver chloride for 2 hours on the steam-bath. After filtering, concentrating, and adding hydrochloric acid, the chloride separates as a mass of pale yellow needles. It is collected, recrystallised from very dilute hydrochloric acid, and left on porous porcelain exposed to the air for 2 days. The chloride then has the composition $C_{20}H_{18}O_4NCl,4\frac{1}{2}$ aq. and, after heating till constant at 105°, still retains $\frac{1}{2}$ aq. (Found: loss at 105° = 16·4. Calc. for the loss of 4 aq., 16·0 per cent.). After drying at 105°, the substance yielded C = 63·0; H = 5·1. $C_{20}H_{18}O_4NCl,\frac{1}{2}$ aq. requires C = 63·0; H =

5·0 per cent.). *ψ-epi*Berberinium chloride is readily soluble in cold water, but only very sparingly soluble in dilute hydrochloric acid; the aqueous solution gives no precipitate on the addition of ammonia.

When this chloride was boiled with much absolute alcohol, it dissolved and, after an hour, the filtered solution deposited the anhydrous salt as a pale yellow, granular deposit of prisms and the supernatant liquid became filled with a mass of long, yellow needles which changed to prisms on touching with a glass rod. It appears therefore to be dimorphous. Before analysis, the substance was left over sulphuric acid in a vacuum desiccator for 2 days (Found: C = 64·3; H = 4·8. $C_{20}H_{18}O_4NCl$ requires C = 64·5; H = 4·8 per cent.).

Moreover, a third modification of the chloride was obtained on two occasions by digesting the iodide with silver chloride and methyl alcohol (95 per cent.). The concentrated filtrate from the silver salts deposited a mass of crystals and, on fractionally crystallising from water, a comparatively sparingly soluble salt separated, leaving the ordinary chloride in solution. After remaining exposed to the air on porous porcelain for some days, this salt had the composition $C_{20}H_{18}O_4NCl,2\frac{1}{2}$ aq. and lost 2 aq. on heating at 105°. The loss of weight of the air-dried salt at 105° was 8·4, whereas $C_{20}H_{18}O_4NCl,2\frac{1}{2}$ aq. losing 2 aq. requires a loss of 8·6 per cent. The salt (dried at 105°) contained C = 62·9; H = 5·0. $C_{20}H_{18}O_4NCl$, $\frac{1}{2}$ aq. requires C = 63·0; H = 5·1 per cent. When this salt was dissolved in boiling, very dilute hydrochloric acid, the chloride containing $4\frac{1}{2}$ aq. separated on cooling.

It is curious that, in both preparations, the chloride containing $2\frac{1}{2}$ aq. dissolved in cold concentrated sulphuric acid with a deep green coloration, but this property disappeared after two crystallisations from dilute hydrochloric acid.

The Chloroplatinate.—This substance is obtained as a pale ochre, amorphous precipitate when platinic chloride is added to the warm aqueous solution of the chloride. Two specimens were prepared, (i) from the chloride containing $4\frac{1}{2}$ aq. and (ii) from the chloride with $2\frac{1}{2}$ aq. [Found: (i) C = 44·8; H = 3·6; Pt = 18·1. (ii) C = 44·5; H = 3·5; Pt = 18·3. $(C_{20}H_{18}O_4N)_2PtCl_6$ requires C = 44·4; H = 3·3; Pt = 18·1 per cent.].

The *picrate* was obtained by adding aqueous picric acid to the hot aqueous solution of the chloride, in yellow flocks which were crystallised from acetic acid, in which the substance is sparingly soluble. It is evidently dimorphous, since it separates both in rhombs and in bright yellow, curved needles, the latter being the stable modification. After drying at 105°, the picrate melted at

237—238° (Found: C = 53·9; H = 3·9. $C_{20}H_{19}O_5N,C_6H_3O_7N_3$ requires C = 53·6; H = 3·8 per cent.).

Oxy-ψ-epiberberine (VIII) *and Dihydro-ψ-epiberberine* (IX).

When a little potassium hydroxide (20 per cent.) is added to a cold saturated solution of *ψ-epi*berberinium chloride, the yellow colour becomes paler but no precipitate separates and, on adding a further quantity of the alkali, the whole sets to a jelly. On warming, a clear solution is momentarily formed, but this soon clouds owing to the separation of a mixture of oxy-*ψ-epi*berberine and dihydro-*ψ-epi*berberine. In preparing these substances, a boiling solution of the chloride (10 gms.) in water (100 c.c.) was added to a hot solution of potassium hydroxide (40 gms.) in water (60 c.c.) and the whole heated on the steam-bath for 3 hours. The yellow mass which had separated was collected, ground, and extracted four times with small quantities of dilute hydrochloric acid; the residue was then dissolved in hot acetic acid mixed with an equal volume of boiling water, when an almost colourless, satiny mass of *oxy-ψ-epiberberine* rapidly separated (Found: C = 68·3; H = 4·8. $C_{20}H_{17}O_5N$ requires C = 68·4; H = 4·8 per cent.). *Oxy-ψ-epiberberine* melts at 206° (compare oxy*epi*berberine, m. p. 240—241°; *loc. cit.*, p. 518), is sparingly soluble in the usual solvents with the exception of glacial acetic acid, and does not dissolve in dilute acids. The solution in concentrated sulphuric acid is pale yellow with a pale green fluorescence and, on addition of a crystal of potassium nitrate, the colour becomes at first green and then an intense blue.

Dihydro-ψ-epiberberine.—The hydrochloric acid extract from the crude oxy-*ψ-epi*berberine was mixed with concentrated hydrochloric acid, when a mass of bright yellow crystals immediately began to separate. After standing for some hours, this hydrochloride was collected, recrystallised, dissolved in warm water, and precipitated by ammonia. The precipitate was collected, washed well, and twice crystallised from acetone, from which the substance separated in yellow, rhombic prisms (Found: C = 70·9; H = 5·8. $C_{20}H_{19}O_4N$ requires C = 71·2; H = 5·6 per cent.).

Dihydro-*ψ-epi*berberine melts at 173° (compare dihydro*epi*berberine, m. p. 172°; *loc. cit.*, p. 518) and is rather sparingly soluble in alcohol, but more soluble in benzene, and readily soluble in chloroform, yielding pale yellow solutions which exhibit a faint green fluorescence. It is a strong base and forms pale yellow, crystalline salts, of which the *hydrochloride* crystallises in silky, yellow needles, is rather sparingly soluble in dilute hydrochloric acid, and melts at about 266° to a red froth.

The *hydriodide*, $C_{20}H_{19}O_4N,HI$, is obtained by adding potassium iodide to the aqueous solution of the hydrochloride as a yellow, crystalline powder, which is very sparingly soluble even in boiling water (Found: C = 52·1; H = 4·5. $C_{20}H_{20}O_4NI$ requires C = 51·6; H = 4·3 per cent.). It melts at about 281° with blackening.

The solution of the base in concentrated sulphuric acid is pale yellow and, on the addition of a crystal of potassium nitrate, a transient bright green colour results which soon passes into deep orange-brown.

We wish to thank Mr. Fred Hall for carrying out the whole of the analyses required during this investigation. One of us (J. S. B.) desires to express his gratitude to the Royal Commissioners of the 1851 Exhibition for a scholarship which has enabled him to take part in this research; the other (W. H. P.) is indebted to the Government Grant Committee of the Royal Society for a grant which has covered much of the expense of this investigation.

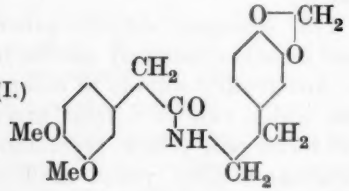
THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, June 10th,* 1924.]

CCXIX.—ψ-*Berberine.*

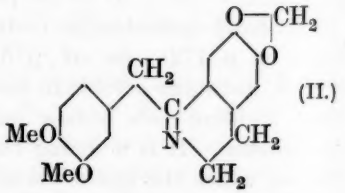
By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, junr., and JOHN RANKIN.

DURING the course of their experiments on the synthesis of tetrahydroberberine, Pictet and Gams (*Ber.*, 1911, **44**, 2480) condensed the chloride of homoveratric acid, $(MeO)_2C_6H_3\cdot CH_2\cdot COCl$, with homopiperonylamine, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NH_2$, and obtained homoveratroyl-homopiperonylamine (I). This substance was converted, by the action of phosphorus pentoxide in boiling xylene, into 1-veratryl-6 : 7-methylenedioxydihydro*iso*quinoline (II) and this base was then reduced by means of tin and hydrochloric acid to veratrylnorhydrohydrastinine (1-veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline (III).*

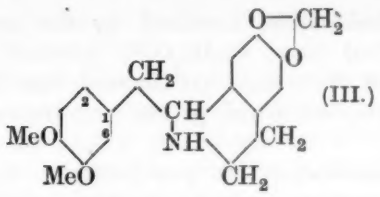
(I.)



(II.)



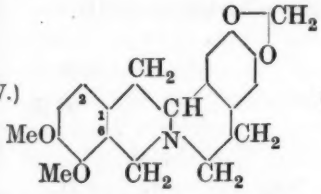
* These formulæ have been rearranged so as to bring them into harmony with similar formulæ in the preceding paper on the synthesis of ψ-*epi*berberine.



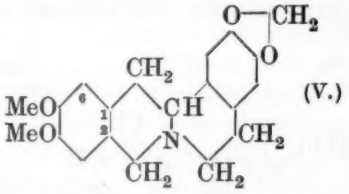
(III.)

The final step was to condense the latter substance with methylal in the presence of hydrochloric acid, when a sparingly soluble hydrochloride was obtained which, on decomposition with potassium carbonate, yielded a base (A) melting at 168° and having the formula $C_{20}H_{21}O_4N$. This condensation with methylal might conceivably take place in two directions, since either the hydrogen atom in the position 2 or that in the position 6 in the formula (III) may take part in the change. In other words, there are two possible formulæ for the base (A), namely (IV) or (V).

(IV.)



and



(V.)

Pictet and Gams claim that the base (A) which they obtained as the result of this ring formation is tetrahydroberberine (IV), but, at the same time, they express surprise that this substance should have been formed and state that their expectation was that the condensation product would prove to be tetrahydro*iso*berberine (V). So far as we are aware, no other case is known of a condensation of this kind taking place in the direction claimed by Pictet and Gams, and the abnormality of the process has been commented on by Jones and Robinson (J., 1917, **109**, 905).

The evidence which Pictet and Gams bring forward in support of their contention that the synthetical base, $C_{20}H_{21}O_4N$, is tetrahydroberberine is as follows :

(i) The base, $C_{20}H_{21}O_4N$, melts at the same temperature as tetrahydroberberine (168°) and there was no depression in melting point when it was mixed with a specimen of tetrahydroberberine.

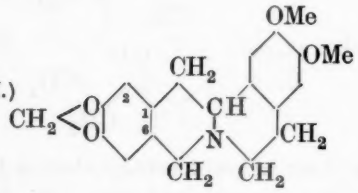
(ii) The base, $C_{20}H_{21}O_4N$, behaved on treatment with bromine or dilute nitric acid exactly like tetrahydroberberine and yielded salts which direct comparison proved to be identical with those of berberine. The picrate melted at 239—240° and, when mixed with the picrate of berberine, there was no depression in melting point.

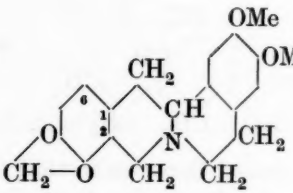
(iii) The hydrobromide, obtained by the action of bromine on the synthetical base, $C_{20}H_{21}O_4N$, behaved exactly like the hydrobromide of berberine and showed the characteristic conversion into oxyberberine (m. p. 199°) on treatment with sodium hydroxide.

In the communication on *ψ-epi*berberine which immediately precedes the present one, it is clearly proved that the condensation of 1-homopiperonyl-6 : 7-dimethoxytetrahydro*iso*quinoline with methylal (or formaldehyde) does not take place abnormally in the direction claimed by Pictet and Gams in their experiments on the synthesis of tetrahydroberberine, but gives rise to a base, $C_{20}H_{21}O_4N$, which is isomeric with tetrahydro*epi*berberine and which we have named tetrahydro-*ψ-epi*berberine.

In other words, the condensation in this case takes place with the assistance of the hydrogen atom (6) of the veratryl nucleus and not with the aid of the hydrogen atom (2), and the result is tetrahydro-*ψ-epi*berberine (VI) and not tetrahydro*epi*berberine (VII).

(VI.)





(VII.)

In order to find some explanation for this puzzling difference in the direction of two such analogous condensations, we decided to undertake a re-investigation of the synthesis which Pictet and Gams claim leads to tetrahydroberberine. As a result of a long series of careful experiments conducted with very carefully purified material and many times repeated, we have been forced to the conclusion that the process described by Pictet and Gams, carried out under the conditions described in detail in the experimental section of this communication, does not lead to tetrahydroberberine (IV), but to the isomeric base (V), which we have named *tetrahydro-ψ-berberine*. That is to say that the condensation of veratrylnorhydrohydrastinine (III) with methylal has, in our experiments, proceeded in the direction indicated by experience. It is, of course, possible that we have inadvertently used conditions which have differed in some material aspect from those employed by Pictet and Gams, and the decision on this point must be left in the hands of independent investigators.

The following brief account of our experimental results should be

supplemented by reference to the experimental section of this investigation.

Homoveratroyl-homopiperonylamine (I) was, in our first experiments, prepared exactly as described by Pictet and Gams (*loc. cit.*, p. 2482), but we subsequently greatly increased the yield by modifying the process in the manner described on p. 1694. This substance melts at 135—136° and behaves towards solvents in the manner described by Pictet and Gams.

We next converted this base into veratrylmethylenedioxydihydro*iso*quinoline (II) by boiling in xylene solution with phosphorus pentoxide exactly as described by Pictet and Gams, but we afterwards found that the same base is obtained in much better yield by digesting the toluene solution with phosphorus oxychloride. Pictet and Gams describe this base as an amorphous substance melting at 68—70° and yielding indefinite salts.

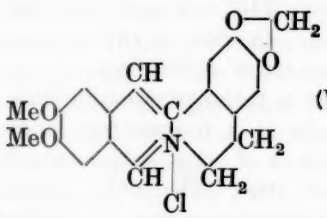
We find, on the contrary, that the base—whether prepared with the aid of pentoxide or oxychloride of phosphorus—is a crystalline substance melting at 88° and yielding well-characterised salts, of which the hydrochloride, hydriodide, and picrate have been prepared and the last two analysed. When this dihydro*iso*quinoline was reduced with tin and hydrochloric acid, it yielded veratrylnorhydrohydrastinine (III), and this crystallises from alcohol in long prisms melting at 84° and yields beautifully crystalline salts, of which the hydrochloride, sulphate, and picrate have been prepared. Pictet and Gams (*loc. cit.*, p. 2483), on the other hand, describe this base as melting at 208—210° and state that the salts in general are difficult to crystallise. In view of this curious discrepancy in the description of the properties of this base, it may be mentioned that it is improbable that a tetrahydro*iso*quinoline of the type under discussion would melt at a temperature approaching 208—210°, since all the substances of this nature which have so far been obtained melt below 100°. The only apparent exception was the so-called tetrahydropapaverine of Goldschmiedt (*Monatsh.*, 1886, **7**, 745; 1898, **19**, 324), which melts at 201—202°, but Pyman (J., 1909, **95**, 1610; 1910, **97**, 1320; 1915, **107**, 176) was able to show that this substance is in reality an abnormally constituted dihydropapaverine and named it "pavine." When veratrylnorhydrohydrastinine (m. p. 88°) was heated on the steam-bath with methylal and concentrated hydrochloric acid, exactly under the conditions described by Pictet and Gams (*loc. cit.*, p. 2484), a sparingly soluble, crystalline hydrochloride separated which, on decomposition with alkali, yielded a base, $C_{20}H_{21}O_4N$, crystallising well from alcohol and melting at 177°, whereas tetrahydroberberine

melts at 169°. Moreover, a mixture of this base with a sample of pure tetrahydroberberine melted at 142—144°, so that there can be no question of identity. This isomeride of tetrahydroberberine we have named *tetrahydro-ψ-berberine.**

In the experiment just described, the yield of tetrahydro-ψ-berberine was small and considerable quantities of an amorphous substance were produced which was carefully examined, but we were unable to detect even a trace of tetrahydroberberine in this material. It was then found that a very much better yield of tetrahydro-ψ-berberine may be obtained by employing a modification of Decker's method (*Annalen*, 1913, **395**, 282) for the synthesis of *iso*quinoline derivatives. A methyl-alcoholic solution of veratrylnorhydrohydrastinine is warmed for a few minutes with formalin and the product poured into water. The intermediate semi-solid formyl derivative is readily converted into tetrahydro-ψ-berberine hydrochloride by warming with concentrated hydrochloric acid, the yield being at least 60 per cent. of that theoretically possible. In this case also, the base melted at 177°.

*The ψ-Berberinium Salts, Oxy-ψ-berberine and Dihydro-ψ-berberine.**

Tetrahydro-ψ-berberine is readily oxidised by iodine with the formation of *ψ-berberinium iodide*, which is sparingly soluble, crystallises well, melts at 274° with decomposition, and is converted on digesting with water and silver chloride into *ψ-berberinium chloride*,

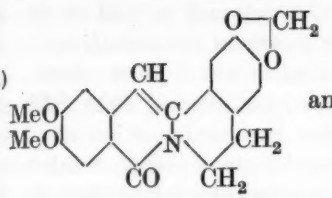


(VIII.)

Crystallised from water, this salt has the composition $C_{20}H_{18}O_4NCl,4\frac{1}{2}$ aq. and, on drying at 120°, $\frac{1}{2}$ aq. still remains. When, however, the substance is recrystallised from absolute alcohol, the anhydrous chloride is obtained and this separates in very pale yellow needles which darken at 270° and melt at 300°. The *picrate* crystallises in yellow needles and melts and decomposes at 305°, whereas berberinium picrate melts at 239°.

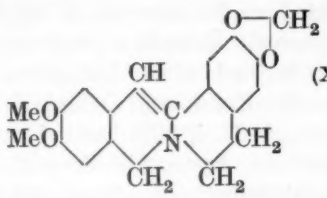
* Strictly speaking, these substances should be named tetrahydroanhydro-ψ-berberine and dihydroanhydro-ψ-berberine, but we have employed the usual names in this communication.

Oxy-ψ-berberine and *dihydro-ψ-berberine*,



(IX)

and



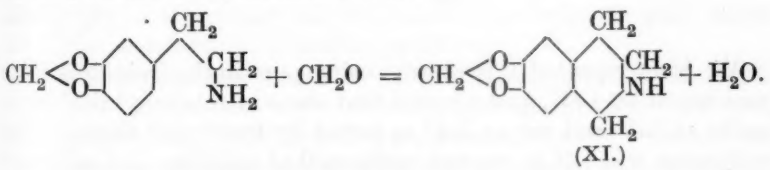
(X.)

are readily obtained when ψ-berberinium chloride is warmed with aqueous potassium hydroxide. Oxy-ψ-berberine crystallises well from dilute acetic acid in nearly colourless needles and melts at 268° (oxyberberine melts at 200°). Dihydro-ψ-berberine also crystallises well in yellow prisms melting at 167° (dihydroberberine melts at 169°) and yields a characteristic hydrochloride melting with decomposition at 255°.

During the course of these experiments we have also re-investigated the process by which Pictet and Gams (*Ber.*, 1911, **44**, 2036) claim to have synthesised oxyberberine with a view to the extension of this method to the synthesis of alkaloids allied to berberine. It was shown by one of us (Perkin, J., 1918, **113**, 764) that oxyberberine may be reduced electrolytically to tetrahydroberberine, which may then, by the action of oxidising agents, be converted into salts of berberine; consequently a synthesis of oxyberberine is also a synthesis of berberine.

If, then, the isomerides of oxyberberine could be synthesised by a similar process, these should be capable of conversion into the known and unknown isomerides of berberine in which we are interested.

The starting point in the Pictet and Gams experiments on the synthesis of oxyberberine was methylene-6 : 7-dioxytetrahydro*iso*-quinoline (norhydrohydrastinine), which those authors obtained by condensing the hydrochloride of homopiperonylamine with methylal in the presence of hydrochloric acid :



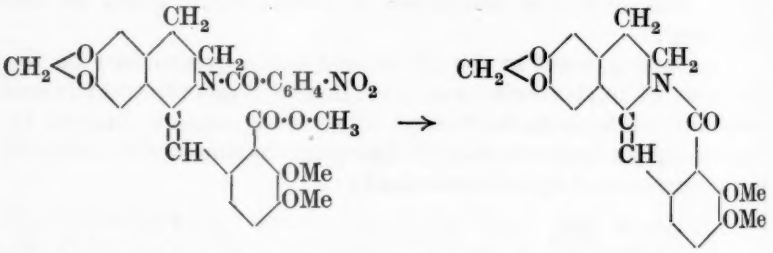
(XI.)

They describe the base as an oil distilling at 197—199°/50 mm. and yielding a hydrochloride melting at 255—257°. On repeating the process of Pictet and Gams, we obtained an oily mixture of bases from which we succeeded in isolating a small quantity of a

hydrochloride melting at 275°, and this, on treatment with alkali, yielded a solid base which crystallised well and melted at 80—81°. Apparently there is a tendency for methylal condensations of this type to lead to the formation of a mixture of bases since, quite recently, Kondo and Ochiai (*J. Pharm. Soc. Japan*, 1923, **313**, 219; Abstr., 1923, i, 837) have shown that the condensation of phenylethylamine hydrochloride with methylal gives rise to a mixture of several substances from which considerable quantities of di-β-phenylethylaminomethane, $CH_2(NH\cdot CH_2\cdot CH_2Ph)_2$, were isolated. In 1913 (*Annalen*, **395**, 354), Decker and Becker discussed the Pictet and Gams synthesis of norhydrohydrastinine and showed that, if the methylal is replaced by formaldehyde (*loc. cit.*, p. 351), a good yield of methylenehomopiperonylamine,

$$CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot N{:}CH_2,$$

is obtained, and they describe the almost quantitative conversion of this substance into norhydrohydrastinine by warming with hydrochloric acid. These investigators state that the base melts at 81—83° and yields a hydrochloride melting at 274—276°, constants which are in close agreement with those observed by us. The next step in the Pictet and Gams synthesis of oxyberberine was the conversion of the crude norhydrohydrastinine into the *o*-nitrobenzoyl derivative, which they describe as melting at 104°. A mixture of this derivative and the methyl ester of opianic acid was left for 14 days in contact with concentrated sulphuric acid and, on heating the condensation product with alcoholic potassium hydroxide (15—20 per cent.) at 140—150° oxyberberine was obtained.



We have repeated this process using pure norhydrohydrastinine melting at 80—81°, and we find that the *o*-nitrobenzoyl derivative melts at 154° and not at 104° as stated by Pictet and Gams. This substance was left in contact with methyl opianate and sulphuric acid in the manner described by Pictet and Gams and yielded a brown solid from which nothing crystalline could be obtained. When this was heated at 140—150° with alcoholic potassium hydroxide (15—20 per cent.), we failed, in spite of careful search, to detect the presence even of traces of oxyberberine. In view of the work

of Späth and Lang (*Ber.*, 1921, **54**, 3071), during the course of which it was shown that tetrahydroberberine is decomposed on heating in a sealed tube with 20 per cent. methyl-alcoholic potassium hydroxide at 180° with elimination of the methylene group, it seemed improbable that oxyberberine could be produced under the conditions just mentioned. In order to test this view, pure oxyberberine was heated with alcoholic potassium hydroxide (15 per cent.) at 140° for 2 hours, as the result of which it was completely decomposed with the formation of a phenolic substance which was soluble in aqueous alkali and was readily oxidised in contact with air. We are, at the present time, engaged in the careful examination of the product of this decomposition.

EXPERIMENTAL.

3 : 4-*Dimethoxyphenylpyruvic Acid*, $(MeO)_2C_6H_3\cdot CH_2\cdot CO\cdot CO_2H$.—This acid was prepared from 3 : 4-dimethoxybenzaldehyde (veratraldehyde) by Kropp and Decker's method (*Ber.*, 1909, **42**, 1186), but the separation of the pyruvic acid from benzoic acid was greatly facilitated in the following way. The alkaline solution from the hydrolysis of the azlactone, containing the mixed acids, was cooled and saturated with sulphur dioxide when the benzoic acid was precipitated and removed by filtration.

The filtrate, containing the bisulphite derivative of the pyruvic acid, was made strongly acid with hydrochloric acid and heated on the steam-bath for several hours, when, on standing, nearly pure 3 : 4-dimethoxyphenylpyruvic acid separated. After one crystallisation from glacial acetic acid, it melted at 187° and the yield, calculated from the dimethoxybenzaldehyde employed, was about 50 per cent. of the theoretical.

3 : 4-*Dimethoxyphenylacetic Acid* $(MeO)_2C_6H_3\cdot CH_2\cdot CO_2H$.—This acid was obtained in a yield of 70 per cent. by oxidising 3 : 4-dimethoxyphenylpyruvic acid in alkaline solution with hydrogen peroxide, essentially as recommended by Cain, Simonsen, and Smith (J., 1913, **103**, 1036) for the preparation of *p*-methoxyphenylacetic acid. After drying in a desiccator, it melted at 98°.

3 : 4-*Methylenedioxycinnamic Acid*, $CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH\cdot CO_2H$, *and its Conversion into* 3 : 4-*Methylenedioxyphenylethylamine*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NH_2$.—When piperonal (5 parts), fused sodium acetate (3 parts), and acetic anhydride (6 parts) were heated at 180° for 6 hours in a reflux apparatus, a 30 per cent. yield of the cinnamic acid was obtained, but for the preparation of large quantities of material the following method was found to be much more advantageous. Piperonal (100 gms.) and malonic acid (150 gms.) dissolved in pyridine (300 c.c.) and piperidine (5 c.c.), were heated

for an hour on the steam-bath, when a rapid elimination of carbon dioxide took place and the reaction was completed by boiling the solution for 5 minutes.* The product was cooled, poured into water, and the almost quantitative yield of pure 3 : 4-methylenedioxycinnamic acid (m. p. 233°) collected. 3 : 4-Methylenedioxyphenylpropionic acid was prepared in a yield of 85 per cent. from this cinnamic acid by reduction with sodium amalgam as described by Perkin and Robinson (J., 1907, **91**, 1079). 3 : 4-*Methylenedioxyphenylpropionamide*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CONH_2$. This derivative proved to be difficult to prepare, but ultimately the following method was found to give excellent results. The acid (100 gms.), dissolved in chloroform (340 c.c.), is allowed to react for 12 hours with thionyl chloride (74 c.c.) at the room temperature and the product is then poured into a solution containing sodium hydroxide (50 gms.) and concentrated ammonia (1200 c.c.). The chloroform is removed by distillation and, after filtering from traces of tar, the filtrate is cooled, when the amide (100 gms.) separates in a state sufficiently pure for the next operation. The conversion into 3 : 4-*methylenedioxyphenylethylamine* was brought about by treatment with sodium hypochlorite essentially as recommended by Decker (*Annalen*, 1915, **395**, 291) in the case of the preparation of homopiperonylamine and the yield was about 50 per cent. of the theoretical.

Homoveratroyl-homopiperonylamine (I).—(i) 3 : 4-Dimethoxyphenylacetyl chloride was prepared by dissolving the acid (10 gms.) in chloroform (30 c.c.) and boiling with thionyl chloride (10 gms.) until the evolution of hydrogen chloride had ceased. The chloroform and excess of thionyl chloride were removed by distillation and the residual syrup was gradually added to a suspension of 3 : 4-methylenedioxyphenylethylamine (8 gms.) in 10 per cent. potassium hydroxide solution. The mixture was shaken vigorously and cooled, when the homoveratroylhomopiperonylamine gradually solidified and, after shaking for 3 hours, the solid was collected, recrystallised from alcohol, and obtained in a yield of 6 grams.

(ii) 3 : 4-Methylenedioxyphenylethylamine (24 gms.) and 3 : 4-dimethoxyphenylacetic acid (28·5 gms.) were heated under reflux for 6 hours at 180°. The mixture was dissolved in a little boiling alcohol and, on cooling, 35 gms. of homoveratroyl-homopiperonylamine separated. Prepared by either of these methods, this substance melted at 135—136° and had all the properties ascribed to it by Pictet and Gams (*loc. cit.*, p. 2482).

1-*Veratryl*-6 : 7-*methylenedioxydihydroisoquinoline* (II).—In our earlier experiments, this substance was prepared from homo-

* This method was suggested to us by Professor R. Robinson.

veratroyl-homopiperonylamine by dehydration with phosphorus pentoxide in boiling xylene as described by Pictet and Gams (*loc. cit.*, p. 2482). The ethereal extract gradually deposited the dihydro*iso*quinoline in colourless prisms, m. p. 86—87°. The yield was, however, very small and the ether mother-liquors, on concentration, deposited a basic substance which, after crystallisation from alcohol, melted at 150—151° (see below); about 20 per cent. of the amine was recovered unchanged from the xylene solution.

A much better method for the preparation of this base is as follows: Homoveratroyl-homopiperonylamine (6 gms.), dissolved in toluene (30 c.c.), is boiled for 1½ hours with phosphorus oxychloride (12 c.c.). The solution is cooled, diluted with light petroleum (b. p. 80—100°), the solvent decanted, the residual syrup dissolved in a little hot alcohol, made alkaline by the addition of alcoholic potassium hydroxide, and poured into a large bulk of water. On standing, the dihydro*iso*quinoline separates in small, colourless needles in a yield of 75 per cent. of the theoretical.

1-Veratryl-6 : 7-methylenedioxydihydro*iso*quinoline melts at 87—88° and is soluble in benzene, acetone, or chloroform, sparingly soluble in ether or petroleum, and insoluble in water. The *hydrochloride* separates from the concentrated aqueous solution of the base in dilute hydrochloric acid in pale yellow prisms containing water of crystallisation and melting at 62°. After drying over phosphorus pentoxide in a vacuum, the crystals are opaque and paler in colour and melt at 125°. The dry substance rapidly absorbs moisture on exposure to air, again becoming yellow and melting at 62°. The *hydriodide* is precipitated, on the addition of potassium iodide to the aqueous solution of the hydrochloride, as a crystalline mass which separates from alcohol or water in pale yellow prisms, m. p. 239—240° (Found : C = 50·5; H = 4·3. $C_{19}H_{20}O_4NI$ requires C = 50·3; H = 4·3 per cent.). The *picrate* was obtained by mixing alcoholic solutions of the base and picric acid and crystallises from glacial acetic acid in small, yellow needles, m. p. 206° (Found : C = 54·0; H = 3·9. $C_{25}H_{22}O_{11}N_4$ requires C = 54·1; H = 4·0 per cent.). The base is characterised by a remarkable tendency to undergo oxidation with the formation of a new crystalline base, $C_{19}H_{17}O_5N$, melting at 151°. This oxidation takes place when alcoholic, ether or benzene solutions of the base are exposed to the air for a few hours, but does not appear to occur in acid solution. This new base is being subjected to detailed examination, the results of which will be submitted in a future communication.

1-*Veratryl*-6 : 7-*methylenedioxytetrahydroisoquinoline* (III).—This substance is prepared by dissolving the dihydro*iso*quinoline (II) in

concentrated hydrochloric acid and boiling in a reflux apparatus with a large excess of granulated tin. After a few minutes, the sparingly soluble tin double salt of the dihydro*iso*quinoline separates and, to complete the reduction, it is necessary to redissolve this by the addition of alcohol. After 12 hours, the colourless solution is decanted from the tin, the alcohol evaporated, and the solution cooled, when the colourless tin double salt of the tetrahydro*iso*quinoline separates and is collected and washed. It is then dissolved in boiling water, filtered from traces of yellow impurity, the tin removed as sulphide, and the filtrate concentrated until the hydrochloride of the tetrahydro*iso*quinoline commences to separate. This is collected, dissolved in hot water, and decomposed with sodium hydroxide, when an oily base separates which rapidly solidifies and crystallises from alcohol in elongated prisms (Found: C = 69·5; H = 6·4. $C_{19}H_{21}O_4N$ requires C = 69·7; H = 6·4 per cent.).

1-Veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline is soluble in the usual solvents with the exception of petroleum, crystallises readily, and melts at 84°. The *hydrochloride* separates from water in beautiful, colourless, rectangular prisms which melt to a clear liquid at 236°. It is sparingly soluble in cold water and alcohol and particularly so in dilute hydrochloric acid (Found: C = 62·7; H = 5·9. $C_{19}H_{21}O_4N,HCl$ requires C = 62·7; H = 6·0 per cent.). The *sulphate* crystallises from water in colourless plates, m. p. 136—137°, and is soluble in boiling alcohol. The *picrate*, prepared in alcoholic solution, crystallises from alcohol in long, bright yellow needles melting, with slight decomposition, at 185—187°.

Tetrahydro-ψ-berberine (VI).

Two methods were employed in the synthesis of this substance. (i) 1-Veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline (5 gms.), dissolved in concentrated hydrochloric acid (25 c.c.), was heated on the steam-bath for 1½ hours during the gradual addition of methylal (8 gms.). The sparingly soluble hydrochloride soon commenced to separate in the hot solution and, after cooling, was collected, dissolved in hot water, and converted into the base by decomposition with sodium hydroxide. This separated as an oil which rapidly solidified and the crude product was dissolved in alcohol, mixed with ether, and the alcohol removed by washing several times with water. The ethereal solution was dried over potassium carbonate, concentrated, and then allowed to evaporate slowly, when small needles of *tetrahydro-ψ-berberine* gradually separated. After recrystallisation from alcohol, the substance melted at 177.°

The hydrochloric acid mother-liquors were made slightly alkaline

with sodium hydroxide, when large quantities of a dark-coloured, amorphous base separated. This was sparingly soluble in alcohol or ether, but no tetrahydroberberine could be isolated by extracting with ether in a Soxhlet apparatus. The extract consisted of a white, amorphous, high-melting substance of unknown composition and our experience is that similar substances are frequently met with in methylal condensations of this type.

(ii) A much better method for the preparation of tetrahydro-ψ-berberine was found to be the following: 1-Veratrylmethylenedioxytetrahydro*iso*quinoline (5 gms.), dissolved in methyl alcohol (10 c.c.), is warmed at about 60° for a few minutes with 40 per cent. formaldehyde solution (10 c.c.). The product is mixed with water, the solution decanted from the syrup, and this freed from formaldehyde by washing several times with water. The syrup is then dissolved in concentrated hydrochloric acid and heated on the steam-bath for a few minutes; the sparingly soluble hydrochloride separates, and increases in amount on cooling. This is collected, dissolved in boiling water, decomposed with sodium hydroxide, and the base recrystallised from alcohol. It then melts at 177° and the yield is 60 per cent. of the theoretical. Careful search in the mother-liquors did not reveal the presence of any trace of tetrahydroberberine.

Tetrahydro-ψ-berberine crystallises in small needles melting sharply at 177°. It is sparingly soluble in ether, but readily soluble in benzene, chloroform, acetone, or hot alcohol. It dissolves in concentrated sulphuric acid to a pale yellow solution which becomes greenish-brown and then red on the addition of a crystal of potassium nitrate. When mixed with a specimen of tetrahydroberberine which had been prepared by the reduction of berberinium chloride and melted at 169—170°, a depression in melting point of 26° was observed (Found: C = 70·5; H = 6·4. $C_{20}H_{21}O_4N$ requires C = 70·8; H = 6·2 per cent.).

The *hydrochloride* is sparingly soluble in cold water and particularly so in dilute hydrochloric acid, but can be crystallised from much hot water, from which it separates in small, colourless, elongated prisms which soften and darken at 222° and melt at 228—230°. The *hydriodide* is immediately precipitated by the addition of potassium iodide to a hot aqueous solution of the hydrochloride. It is very sparingly soluble in hot water, from which it crystallises in small prisms which soften at 170° and decompose at 222°. The *sulphate* is sparingly soluble in cold water and crystallises from hot water in long, slender needles melting at 168°. The *picrate* separates in bright yellow needles melting at 176° when an alcoholic solution of picric acid is added to the hot alcoholic

solution of tetrahydro-ψ-berberine. The *methiodide* is obtained by boiling the base with methyl iodide for ½ hour; the excess of methyl iodide is removed by distillation and the residual methiodide crystallised from much hot water, from which it separates in rosettes of prismatic needles melting at 256° and decomposing at 260°.

The ψ-Berberinium Salts.

ψ-Berberinium Iodide.—This quaternary salt is readily obtained in the following manner: Tetrahydro-ψ-berberine (3 gms.), dissolved in ethyl alcohol (100 c.c.) containing potassium acetate (4 gms.), is heated to boiling and a 2 per cent. alcoholic solution of iodine (250 c.c.) slowly added, when the periodide soon separates as a mass of long, felted, brown needles. After boiling for ½ hour, the whole is cooled, the crystals are collected, suspended in boiling water, and sulphur dioxide is passed, when the iodide separates in yellow needles which are recrystallised from water (Found: C = 51·5; H = 4·1. $C_{20}H_{18}O_4NI$ requires C = 51·8; H = 3·9 per cent.).

ψ-Berberinium iodide is sparingly soluble in boiling alcohol or water, but separates from a large volume of boiling water as a felted mass of long, canary-yellow needles melting with decomposition at about 274°.

ψ-Berberinium Chloride (VIII), was obtained by boiling an aqueous suspension of the iodide with excess of freshly-precipitated silver chloride for 6 hours. After filtering, the filtrate was mixed with hydrochloric acid, when the chloride soon began to separate as a mass of pale yellow needles. This fine salt was crystallised from a little dilute hydrochloric acid and allowed to remain on porous porcelain until air-dry. The substance then had the composition $C_{20}H_{18}O_4NCl,4\frac{1}{2}$ aq. and, after drying at 120°, the composition was $C_{20}H_{18}O_4NCl,\frac{1}{2}$ aq. The loss at 120° was 16·5, whereas that calculated for the loss of $4H_2O$ is 16·0 per cent. The chloride (dried at 120°) gave C = 63·4; H = 5·1, whereas $C_{20}H_{18}O_4NCl,\frac{1}{2}$ aq. requires C = 63·0; H = 5·0 per cent.

This chloride (dried at 120°) was boiled for 3 hours with absolute alcohol, in which it is rather sparingly soluble, and after filtering and allowing to cool slowly, the mass of pale yellow slender needles was left over sulphuric acid in a vacuum desiccator for 2 days. Analysis showed that the salt was then anhydrous (Found: C = 64·3; H = 4·9. $C_{20}H_{18}O_4NCl$ requires C = 64·5; H = 4·8 per cent.). This salt darkens at 270° and decomposes at 300°, and the same behaviour is exhibited by the hydrated salt after drying at 120°. It dissolves in concentrated sulphuric acid, yielding a greenish-yellow solution.

The *picrate*, $C_{20}H_{17}O_4N,C_6H_3O_7N_3,H_2O$, was prepared by adding

an alcoholic solution of picric acid to a hot alcoholic solution of the chloride and rapidly separated as a mass of yellow needles (Found : C = 53·9; H = 3·8. $C_{26}H_{22}O_{12}N_4$ requires C = 53·6; N = 3·8 per cent.). This picrate decomposes at 305° and is sparingly soluble in boiling alcohol or acetic acid. For the sake of comparison, a specimen of berberine picrate was prepared. It melted at 239°, as stated by Pictet and Gams (*loc. cit.*, p. 2485) and yielded on analysis : C = 53·8; H = 3·9 per cent.

Oxy-ψ-berberine (IX) *and Dihydro-α-berberine* (X).

These substances result from the action of alkalis on ψ-berberinium chloride. The chloride, suspended in a large excess of 25 per cent. potassium hydroxide, is heated for 4 hours in a rapidly boiling water-bath. The whole is cooled, diluted with water, filtered, and the residue extracted several times with small quantities of warm dilute hydrochloric acid. The dark brown mass is then dissolved in hot glacial acetic acid and a little hot water added, when, on cooling, oxy-ψ-berberine separates in long, pale buff needles, m. p. 265—266°. A second crystallisation from dilute acetic acid yielded almost colourless needles, m. p. 268° (Found : C = 68·1; H = 4·9. $C_{20}H_{17}O_5N$ requires C = 68·4; H = 4·8 per cent.). *Oxy-ψ-berberine* is sparingly soluble in the usual solvents with the exception of glacial acetic acid. It dissolves in concentrated sulphuric acid to a yellow solution, which becomes green and then purple on the addition of a crystal of sodium nitrate. When it was mixed with a specimen of oxyberberine (m. p. 200°), prepared from berberinium chloride, the mixture melted at about 184—186°.

Dihydro-ψ-berberine.—This substance was isolated in the form of its hydrochloride by adding a large excess of concentrated hydrochloric acid to the combined dilute hydrochloric acid extracts of the crude mixture with oxy-ψ-berberine obtained in the manner described above. After remaining over-night, the pale yellow prisms were collected and purified by dissolving in a little water and precipitating with concentrated hydrochloric acid. This *hydrochloride* of dihydro-ψ-berberine melts with decomposition at 253—255° and is readily soluble in hot water.

Dihydro-ψ-berberine, obtained by adding sodium hydroxide to the aqueous solution of the hydrochloride, was recrystallised from acetone (Found : C = 71·0; H = 5·6. $C_{20}H_{19}O_4N$ requires C = 71·2; H = 5·6 per cent.). It separates from acetone in small, pale yellow needles, m. p. 165—167°, and, when mixed with a specimen of dihydroberberine (m. p. 169°) which had been prepared from berberinium chloride, the mixture melted at about 141—143°.

Norhydrohydrastinine (XI).

In our first experiments on the preparation of this substance, we followed the method recommended by Pictet and Gams (*Ber.*, 1911, **44**, 2042) and by subjecting the mixture of hydrochlorides obtained after the reduction with tin and hydrochloric acid to careful fractionation first from alcohol and then from water, we were able to isolate a small quantity of norhydrohydrastinine hydrochloride, m. p. 275°. When the aqueous solution was decomposed by alkali, the base rapidly solidified; it crystallised from dilute alcohol in needles, m. p. 80—81°.

The mother-liquors of this hydrochloride contain large quantities of secondary bases, but we were unable to isolate any substance from this mixture in a pure condition. We then investigated the process recommended by Decker and Becker (*Annalen*, 1913, **395**, 350) for the preparation of norhydrohydrastinine and with very satisfactory results. Using the quantities recommended by them, we dissolved the homopiperonylamine in a little methyl alcohol, warmed for a few minutes with the 40 per cent. formaldehyde, diluted with water, decanted the liquid from the semi-solid mass which had separated, and washed this well with water. The mass was dissolved in a little 20 per cent. hydrochloric acid and warmed for ½ hour on the steam-bath, when, on cooling, the hydrochloride of norhydrohydrastinine separated in a yield of 70 per cent. of theory. After recrystallisation, the hydrochloride melted at 274—275° and on decomposition with alkali, yielded norhydrohydrastinine as a solid which, after recrystallisation from dilute alcohol, melted at 81—83° as stated by Decker and Becker.

N-o-*Nitrobenzoylnorhydrohydrastinine.*—This substance was prepared by warming a solution of the hydrochloride (6 gms.) in water (25 c.c.) with *o*-nitrobenzoyl chloride (6 gms.) during the gradual addition of a 30 per cent. solution of potassium hydroxide. The mixture was well shaken during this addition and, after about ½ hour, the *o*-nitrobenzoyl derivative separated as an oil which solidified on cooling. It crystallised from alcohol in colourless needles, m. p. 154° (Found: C = 62·7; H = 4·5. $C_{17}H_{14}O_5N_2$ requires C = 62·6; H = 4·3 per cent.).

Condensation with Methyl Opianate.—The methyl opianate was prepared in the way recommended by Bain, Perkin, and Robinson (J., 1914, **105**, 2398). The *o*-nitrobenzoyl derivative (3 gms.) and methyl opianate (2·5 gms.) were dissolved in concentrated sulphuric acid (10 c.c.) and allowed to remain at room temperature for 14 days. The solution developed a brown colour and was gradually converted into a jelly-like mass. This was poured into cold water,

when a brown, amorphous solid separated which could not be purified. It was sparingly soluble in the usual organic solvents, but rapidly dissolved to a brown liquid on warming with a solution of sodium hydroxide. It was precipitated from this solution by mineral acids, but not by carbon dioxide.

This brown solid (1 gm.) was heated with 15 per cent. alcoholic potassium hydroxide for 2 hours in a sealed tube at 140—150° (Pictet and Gams, *loc. cit.*, p. 2044). On diluting with water, the whole dissolved and hydrochloric acid precipitated a brown solid which was collected, dried, and extracted with alcohol in a Soxhlet apparatus. The brown, amorphous residue did not melt at 280° and was insoluble in the usual solvents and also in dilute mineral acids, but dissolved readily and completely in dilute sodium hydroxide to a brown solution and was not precipitated by carbon dioxide. There was clearly no oxyberberine present in this substance. The alcoholic extract was concentrated, when a small quantity of a brown, amorphous solid separated which was completely soluble in dilute sodium hydroxide and therefore did not contain any oxyberberine. On repeating the above experiment, exactly the same results were obtained.

Action of Alcoholic Potassium Hydroxide on Oxyberberine.—Carefully purified and finely powdered oxyberberine (1 gm.) and alcoholic potassium hydroxide (5 c.c. of 15 per cent.) were heated in a sealed tube for 2 hours at 140—150°, when, on cooling, a deposit of bright yellow needles of a potassium derivative was found to have separated. On adding water, the liquid discoloured rapidly in the air, and, as the potassium derivative was also found to be soluble in water, it was obvious that the whole of the oxyberberine had been changed by this treatment. We are at present engaged in an examination of these products of the decomposition of oxyberberine.

We are indebted to Mr. Fred Hall for the whole of the analyses contained in this communication. One of us (R. D. H.) is indebted to the Commissioners of the 1851 Exhibition for a scholarship which has enabled him to take part in this research. A part of the heavy expense of the investigation has been met by a grant from the Royal Society.

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CCXX.—*The Reactions of Thiocarbonyl Chloride. Part I. Reaction with Aromatic Primary Amino-compounds.*

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The ordinary method for the preparation of symmetrically di-substituted thiocarbamides, and from them the thiocarbimides, by the action of carbon disulphide and alcoholic alkali on the appropriate amine, is not applicable when the amine is substituted in the nucleus by halogen or by nitro- or hydroxyl-groups, the yields being poor, and separation from the by-products difficult. It was of interest, therefore, to determine whether the reaction between thiocarbonyl chloride and aromatic amino-compounds, investigated by Rathke (*Ber.*, **1873**, **5**, 799) in the case of aniline, $NH_2Ph+CSCl_2=NPhCS+2HCl$, could be successfully applied to such cases.

We find that this reaction takes place in stages; first, the formation of a thiocarbamyl chloride by the addition of a molecule of thiocarbonyl chloride to the nitrogen atom followed by the loss of a molecule of hydrogen chloride, and secondly, the loss of a further molecule of hydrogen chloride, to give the thiocarbimide:

$$NH_2Ph+CSCl_2 \longrightarrow \underset{\text{(I.)}}{[NH_2PhCl\cdot CSCl]} \longrightarrow \underset{\text{(II.)}}{NHPh\cdot CSCl} \longrightarrow NPhCS.$$

The compound II was isolated and examined.

The replacement of a primary by a secondary amine in this reaction (*Bull. Soc. chim.*, 1910, [iv], **7**, 989) causes the reaction to stop short at the thiocarbamyl chloride stage, and the thiocarbamyl chlorides from such amines as methylaniline or ethylaniline are quite stable, and can be recrystallised from ether.

When, under suitable conditions, the aniline (or other amine) is in excess of the thiocarbonyl chloride, the thiocarbamyl chloride, or its decomposition product, the thiocarbimide reacts with the excess of amine to give a symmetrical thiocarbamide, thus:

$$NHR\cdot CSCl+NH_2R \xrightarrow{-HCl} CS(NHR)_2 \longleftarrow NRCS+NH_2R.$$

The best way of conducting these reactions is in aqueous suspension. To prepare the thiocarbimide the amine was slowly added with shaking to an equal weight of thiocarbonyl chloride suspended in water and after a while the mixture was distilled in steam. The first 10 c.c. were collected separately, being contaminated with excess of thiocarbonyl chloride; the oil in the remainder of the distillate was practically pure thiocarbimide,

and in almost every case a good yield was obtained. The thiocarbimides were identified by their physical properties, and by converting them into the corresponding thiocarbamides by boiling with aqueous-alcoholic ammonia.

The symmetrically di-substituted thiocarbamides were prepared by heating a mixture of the amine (2 mols.), suspended in water, and thiocarbonyl chloride (1 mol.), under reflux until the orange-red drops of thiocarbonyl chloride no longer appeared in the condenser tube. Potassium carbonate (1 mol.) was now added to set free the amine, heating was continued for several hours, the mixture cooled, and the cake of the substituted thiocarbamide ground up with dilute hydrochloric acid, washed with water, and recrystallised until the melting point was constant.

Thiocarbimides and thiocarbamides were prepared by this method from amino-compounds substituted in the nucleus by alkyl, halogen, nitro-, hydroxyl, and carbethoxyl groups, and it was observed that the reaction proceeded with equal ease when the substituent was a nitro-, halogen or hydroxyl group, as when an alkyl substituent was present, and was independent of the position of the substituted group. With di-*o*-substituted amines, the substituents being two halogen atoms or two nitro-groups, no reaction took place (2 : 6-dibromoaniline, 2 : 4 : 6-tribromoaniline, 2 : 4 : 6-tri-iodoaniline, and 2 : 4 : 6-trinitroaniline) although with mesidine, nitromesidine, 2 : 6-dihydroxyaniline, and 2 : 6-dimethoxyaniline the reaction proceeded normally.

The reaction proceeded extremely easily with amines in which the amino-group was substituted in the aliphatic side-chain (α- and β-phenylethylamines and benzylamine).

The yields by this method were usually almost quantitative, and the products singularly free from impurities, and were it not for the expensive and objectionable nature of thiocarbonyl chloride, the method would have considerable synthetic interest.

Experimental.

Thiocarbonyl chloride was prepared by Frankland, Garner, and Challenger's method (*J. Soc. Chem. Ind.*, 1920, **39**, 256T). Carbon disulphide was directly chlorinated in presence of a trace of iodine to thiocarbonyl perchloride, which was purified and reduced to thiocarbonyl chloride by tin and hydrochloric acid. In the removal of sulphur chloride from the chlorination mixture, the yield of thiocarbonyl perchloride was considerably increased by allowing the crude product to drop into a large flask through which a rapid current of steam was passing. To this flask was attached a glass column, 80 cm. long and 2·5 cm. in diameter, filled with beads,

into which a rapid current of steam was led at a point 40 cm. from the top. The mixture of thiocarbonyl perchloride vapour and steam which issued from this column was condensed and treated as in the original method. The whole of the sulphur chloride was removed in the step just described, thus avoiding the second steam distillation required by the older method.

Phenylthiocarbamyl Chloride, $C_6H_5{\cdot}NH{\cdot}CSCl$. — An ethereal solution of aniline was added to 10 gms. of thiocarbonyl chloride in 150 c.c. of dry ether, until the orange colour of the latter had nearly disappeared. The white precipitate of phenylthiocarbamyl chloride was washed with dry ether, dried in a vacuum, and preserved in sealed tubes. The white powder decomposed on heating, or instantly in contact with water, with formation of phenylthiocarbimide and hydrogen chloride. On warming with a little aniline, it gave thiocarbanilide, and on heating with mercuric oxide phenylcarbimide was obtained.

Thiocarbimides and Thiocarbamides derived from Primary Amines. —Experiments were made with the amines tabulated below, and as in all cases the reaction proceeded normally, the individual experiments have been summarised in the following table (each m. p. and b. p. is corrected) :

Compound.	Source.	Properties.
o-Tolylthiocarbimide.	*o*-Toluidine.	B. p. 238—240°. Pale, straw-coloured oil, smelling like phenylthiocarbimide.
o-Tolylthiocarbamide.	,,	M. p. 155°. White needles.
s-Di-*o*-tolylthiocarbamide.	,,	M. p. 161°. Fine, snow-white needles. Easily soluble in hot alcohol, but only sparingly so in cold.
m-Tolylthiocarbimide.	*m*-Toluidine.	B. p. 244°. Pale yellow oil, smelling like the *o*-compound.
m-Tolylthiocarbamide.	,,	M. p. 110·5—111·5°. Small, white crystals.
s-Di-*m*-tolylthiocarbamide.	,,	M. p. 111·5—112·5°. Short, white prisms.
p-Tolylthiocarbimide.	*p*-Toluidine.	M. p. 25—26°. White needles, from ether. Pleasant smell resembling aniseed.
p-Tolylthiocarbamide.	,,	M. p. 182°. Fine, white needles.
s-Di-*p*-tolylthiocarbamide.	,,	M. p. 176°. Granular crystals, only moderately soluble in hot alcohol.
*3 : 4-Dimethylphenylthiocarbimide.	3 : 4-Xylidine.	B. p. 263—264°. Pale, yellow oil, smelling of aniseed.
*3 : 4-Dimethylphenylthiocarbamide.	,,	M. p. 141·5—142·5. Small, white needles readily soluble in alcohol.

* Compounds marked with an asterisk appear to be new.

Compound.	Source.	Properties.
s-Di-3 : 4-dimethylphenylthiocarbamide.	3 : 4-Xylidine.	M. p. 178·5—179°. Small, white needles.
*2 : 4-Dimethylphenylthiocarbimide.	2 : 4-Xylidine.	M. p. 28—29°. White needles, with a pleasant smell like aniseed.
*2 : 4-Dimethylphenylthiocarbamide.	,,	M. p. 181·5°. Long, silky needles.
s-Di-2 : 4-dimethylphenylthiocarbamide.	,,	M. p. 149—150°. White, microcrystalline powder.
*2 : 5-Dimethylphenylthiocarbimide.	2 : 5-Xylidine.	B. p. 262—263°. Pale, straw-coloured oil, smelling like phenylthiocarbimide.
*2 : 5-Dimethylphenylthiocarbamide.	,,	M. p. 134·5—135·5°. Large, prismatic crystals.
s-Di-2 : 5-dimethylphenylthiocarbamide.	,,	M. p. 148—148·5°. Short, white needles.
*ψ-Cumidylthiocarbimide.	ψ-Cumidine.	M. p. 22—23°. Small, white crystals. Very soluble in alcohol.
*ψ-Cumidylthiocarbamide.	,,	M. p. 167·5—168°. Long, glistening needles.
s-Di-ψ-cumidylthiocarbamide.	,,	M. p. 145·5—146·5°. Very small, white needles.
Mesitylthiocarbimide.	Mesidine.	M. p. 62—63°. Small, white needles with a pleasant flower-like smell.
Mesitylthiocarbamide.	,,	M. p. 220°. Small, white crystals.
s-Dimesitylthiocarbamide.	,,	M. p. 195°. Small, white crystals.
α-Phenylethylthiocarbimide.	α-Phenylethylamine.	B. p. 240—244°. Pale, yellow oil with a strong smell.
β-Phenylethylthiocarbimide.	β-Phenylethylamine.	B. p. 247·5°. Pale yellow oil, with a smell as of watercress.
β-Phenylethylthiocarbamide.	β-Phenylethylamine.	M. p. 138°. Glistening, white plates.
s-Di-β-phenylethylthiocarbamide.	β-Phenylethylamine.	M. p. 90—91°. Short needles.
Benzylthiocarbimide.	Benzylamine.	B. p. 242—243°. Pale yellow oil, smelling like watercress.
Benzylthiocarbamide.	,,	M. p. 164·5—165·5°. Small, glistening crystals.
s-Dibenzylthiocarbamide.	,,	M. p. 147—148°. White crystals, very soluble in alcohol.

Thiocarbimides and Thiocarbamides from Halogen-substituted Primary Amines.—In this group of reactions the presence of a single halogen atom at any position in the nucleus had no effect on the course of the reaction, which proceeded as easily as if the amine was unsubstituted. The following halogen compounds were prepared (each m. p. and b. p. is corrected):

Compound.	Source.	Properties.
o-Chlorophenylthiocarbimide.	*o*-Chloroaniline.	B. p. 260—262°. Clear, colourless liquid, with an unpleasant smell.
o-Chlorophenylthiocarbamide.	*o*-Chloroaniline.	M. p. 146—146·5°. Small, white needles, easily soluble in alcohol.

Compound.	Source.	Properties.
s-Di-*o*-chlorophenylthiocarbamide.	*o*-Chloroaniline.	M. p. 128—129°. Minute, white, felted needles.
m-Chlorophenylthiocarbimide.	*m*-Chloroaniline.	B. p. 249—250°. Colourless oil, with an unpleasant smell.
m-Chlorophenylthiocarbamide.	*m*-Chloroaniline.	M. p. 140—140·5°. Broad, white plates, from alcohol.
s-Di-*m*-chlorophenylthiocarbamide.	*m*-Chloroaniline.	M. p. 131·5°. White crystals easily soluble in alcohol.
p-Chlorophenylthiocarbimide.	*p*-Chloroaniline.	M. p. 45°. White needles, with a pleasant smell of aniseed.
p-Chlorophenylthiocarbamide.	*p*-Chloroaniline.	M. p. 174·5°. Large, white plates from dilute alcohol.
s-Di-*p*-Chlorophenylthiocarbamide.	*p*-Chloroaniline.	M. p. 176°. Small, brilliant needles.
p-Bromophenylthiocarbimide.	*p*-Bromoaniline.	M. p. 60—61°. Snow-white needles with a pleasant smell.
p-Bromophenylthiocarbamide.	*p*-Bromoaniline.	M. p. 183·5—184°. Granular, crystalline powder.
s-Di-*p*-bromophenylthiocarbamide.	*p*-Bromoaniline.	M. p. 188°. Bright needles from alcohol.
p-Iodophenylthiocarbimide.	*p*-Iodoaniline.	M. p. 63°. Hair-like needle crystals, with a faint, but pleasant smell.
p-Iodophenylthiocarbamide.	,,	M. p. 184°. Glistening, white plates.
s-Di-*p*-iodophenylthiocarbamide.	,,	M. p. 183·5—184·5°. Short, blunt, white crystals.
*5-Bromo-*o*-tolylthiocarbimide.	5-Bromo-*o*-toluidine.	M. p. 48—49°. Fine needle-crystals with a pleasant smell.
*5-Bromo-*o*-tolylthiocarbamide.	5-Bromo-*o*-toluidine.	M. p. 186°. Broad, glistening plates.
**s*-Di-5-bromo-*o*-tolylthiocarbamide.	5-Bromo-*o*-toluidine.	M. p. 159°. Short, white needles.

Thiocarbimides and Thiocarbamides from Nitro-substituted Primary Amines.—Although, in this group of reactions, the presence of the nitro-group made the amine more reactive, the compounds obtained tended to decompose into carbon dioxide, hydrogen sulphide, and the original amine, when boiled in an alkaline solution. This decomposition was particularly noticed in the case of *o*-nitrophenylthiocarbimide. In the case of picramide (*s*-trinitroaniline) no reaction took place. The following compounds were prepared (each m. p. is corrected):

Compound.	Source.	Properties.
o-Nitrophenylthiocarbimide.	*o*-Nitroaniline.	M. p. 73—74°. Bright, golden-yellow plates, which turn green on exposure to light,† the green colour disappearing on keeping in the dark. Gives a bluish-violet colour with concentrated sulphuric acid.†

† These phenomena are being investigated.

Compound.	Source.	Properties.
o-Nitrophenylthiocarbamide.	*o*-Nitroaniline.	M. p. 140·5—141·5°. Orange crystals. Gives a mauve colour on warming with concentrated sulphuric acid.†
m-Nitrophenylthiocarbimide.	*m*-Nitroaniline.	M. p. 59—60°. Almost white needles, very soluble in alcohol.
m-Nitrophenylthiocarbamide.	,,	M. p. 120—125° (decomp.). Pale yellow crystals.
s-Di-*m*-nitrophenylthiocarbamide.	,,	M. p. 163·5—164·5°. Small, buff-coloured crystals.
p-Nitrophenylthiocarbimide.	*p*-Nitroaniline.	M. p. 121—122°. Very pale yellow crystals. Easily soluble in alcohol.
p-Nitrophenylthiocarbamide.	,,	M. p. 189—190°. Yellow, crystalline powder.
s-Di-*p*-nitrophenylthiocarbamide.	,,	M. p. 195—196°. Orange-brown, crystalline powder.
5-Nitro-*o*-tolylthiocarbimide.	5-Nitro-*o*-toluidine.	M. p. 55—56°. Lemon-yellow needles.
5-Nitro-*o*-tolylthiocarbamide.	5-Nitro-*o*-toluidine.	M. p. 188·5°. Small, lemon-yellow crystals.
s-Di-5-nitro-*o*-tolylthiocarbamide.	5-Nitro-*o*-toluidine.	M. p. 130—131°. Short, orange-yellow crystals.
Nitromesitylthiocarbimide.	Nitromesidine.	M. p. 74—75°. Pale yellow, hair-like crystals.
Nitromesitylthiocarbamide.	,,	M. p. 199°. Pale yellow, almost white, needles.
s-Di-(nitromesityl)-thiocarbamide.	,,	M. p. 244°. Pale yellow, crystalline powder, only moderately soluble in alcohol.

Thiocarbimides and Thiocarbamides from Hydroxyl-, Alkoxyl-, and Carbethoxyl-substituted Primary Amines.—The reaction proceeded normally with amines containing hydroxyl, alkoxyl, and carbethoxyl groups in the nucleus. A slight modification of the usual method was necessary with amines containing hydroxyl and carbethoxyl groups, since their thiocarbimides were not volatile with steam. In such cases, after removing the excess of thiocarbonyl chloride by steam distillation, the residue was extracted with ether, and the ethereal extract dried over calcium chloride. The thiocarbimide could then be obtained by evaporation of the ether, and fractionation of the residue. In the case of *o*-hydroxyphenylthiocarbimide, and of the thiocarbimide from 2 : 6-dihydroxyaniline, the compounds obtained were those in which migration of the hydrogen had taken place, with the formation of a condensed ring-system, thus, $C_6H_4<^{NCS}_{OH} \longrightarrow C_6H_4<^{N}_{O}>C{\cdot}SH$. In these cases the thiocarbamides could not be prepared by the usual method. The following compounds were prepared (each m. p. and b. p. is corrected) :

Compound.	Source.	Properties.
o-Hydroxyphenylthiocarbimide (stable form).	*o*-Aminophenol.	M. p. 192—193°. White, crystalline needles with a brown tinge.
**m*-Hydroxyphenylthiocarbimide.	*m*-Aminophenol.	Decomposes on heating even at 15 mm. Pale yellow oil, solidifying in the cold to large crystals.
**m*-Hydroxyphenylthiocarbamide.	*m*-Aminophenol.	M. p. 287° with slight decomposition. Pale yellow, crystalline plates.
**s*-Di-*m*-hydroxyphenylthiocarbamide.	*m*-Aminophenol.	Decomposes before melting. Small, white crystals.
**p*-Hydroxyphenylthiocarbimide.	*p*-Aminophenol.	Decomposes before the b. p. is reached. Clear oil, with an unpleasant smell.
p-Hydroxyphenylthiocarbamide.	*p*-Aminophenol.	M. p. 215—216°. Small, white crystals.
s-Di-*p*-hydroxyphenylthiocarbamide.	*p*-Aminophenol.	M. p. 223—224° (decomp.). Small, glistening plates, from hot water.
*2 : 6-Dihydroxyphenylthiocarbimide (stable form).	2 : 6-Dihydroxyaniline.	Decomposes before melting. Minute, white crystals.
p-Methoxyphenylthiocarbimide.	*p*-Anisidine.	B. p. 280—281°. A clear oil, solidifies on standing.
**p*-Methoxyphenylthiocarbamide.	,,	M. p. 210—211°. White, crystalline powder.
s-Di-*p*-methoxyphenylthiocarbamide.	,,	M. p. 186·5°. Small, silvery plates.
**p*-Ethoxyphenylthiocarbimide.	*p*-Phenetidine.	M. p. 75—76°. Large, glistening, white plates.
**p*-Ethoxyphenylthiocarbamide.	,,	M. p. 175—176°. White crystals with a slight pink tinge.
**s*-Di-*p*-ethoxyphenylthiocarbamide.	,,	M. p. 171°. White, nacreous plates.
2 : 6-Dimethoxyphenylthiocarbimide.	2 : 6-Dimethoxyaniline.	M. p. 55°. Small, white needles.
2 : 6-Dimethoxyphenylthiocarbamide.	2 : 6-Dimethoxyaniline.	M. p. 164·5°. Small, white crystals.
**o*-Carbethoxyphenylthiocarbimide.	Ethyl anthranilate.	B. p. 288—290° (slight decomp.). A clear yellow oil, with an unpleasant smell.
**o*-Carbethoxyphenylthiocarbamide.	Ethyl anthranilate.	M. p. 306—308°. White needles.
**s*-Di-*o*-carbethoxyphenylthiocarbamide.	Ethyl anthranilate.	Decomposes before melting. Large, well-defined, white crystals.

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